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Assessment of Large-Scale Photovoltaic Materials Production

Lockheed Missiles and Space Co, Inc, Huntsville, Ala

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ASSESSMENT OF LARGE-SCALE PHOTOVOLTAIC MATERIALS PRODUCTION

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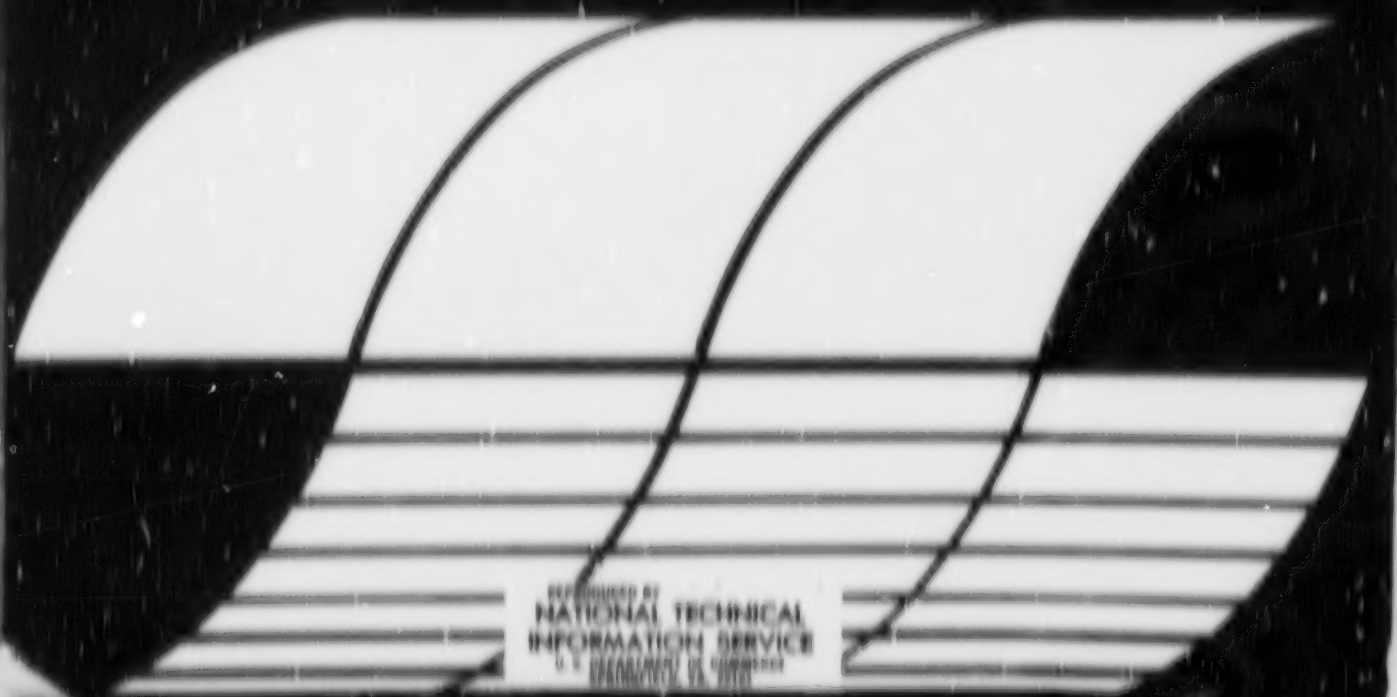

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16. ABSTRACT

Solar cell production at rates needed to supply continuously 1% of projected U.S. power requirements in the year 2000 is examined. Si and CdS are followed from raw material extraction to finished cell; GaAs is reviewed less thoroughly. Numerical data are developed for air, water, and solid wastes, and compared with corresponding effects of equivalent coal-electric power. Mass and energy balance data are derived from flow sheets developed for this report.

For Si, major problems requiring engineering solutions are material and energy inefficiencies. Very large byproduct streams should be eliminated to increase yield by as much as 59% or decrease air pollutant releases by 37% on a process weight basis. Power consumption in cell production creates indirect air pollutant emissions over half as large as those created by the coal-burning plants silicon might replace.

CdS and GaAs are not as energy inefficient. Their metallic raw materials are themselves byproducts of other smelting operations. Atmospheric cadmium releases, and the potential for Cd or As spills are major problem areas.

Of materials known to be involved in cell production, only gallium is resource-limited; however, use of concentrators and thin-film technology may obviate this problem.

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ASSESSMENT OF LARGE-SCALE PHOTOVOLTAIC MATERIALS PRODUCTION

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report assesses the effects of large-scale manufacture of solar photovoltaic materials. It is intended to provide quantitative projections of raw material and energy requirements and waste products, with an assessment of how these affect the environment and natural resources. This report is addressed to those engaged in research and development of photovoltaics and their raw materials and those interested in comparing the promise of solar photovoltaics with other energy sources.

Further information on this subject can be obtained from the Power Technology and Conservation Branch of IERL-Ci.

David G. Stephan
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ABSTRACT

Solar cell production at rates needed to supply continuously 1% of projected U.S. power requirements in the year 2000 is examined. Silicon and cadmium sulfide are followed from raw material extraction to finished cell; gallium arsenide is reviewed less thoroughly. Numerical data are developed for air, water, and solid wastes, and compared with corresponding effects of equivalent coal-electric power. Mass and energy balance data are derived from flow sheets developed for this report.

For Si, major problems requiring engineering solutions are material and energy inefficiencies. A very large byproduct stream should be eliminated to increase yield by as much as 50% or decrease air pollutant releases by 37% on a process weight basis. Power consumption in cell production creates indirect air pollutant emissions over half as large as those created by the coal-burning plants silicon might replace.

The production of cadmium sulfide and gallium arsenide is less energy-intensive. Their metallic raw materials are themselves byproducts of other smelting operations. Atmospheric cadmium releases, and the potential for cadmium or As spills are major problem areas.

Of materials known to be involved in cell production, only gallium is resource-limited; however, use of concentrators and thin-film technology may obviate this problem.

This report was submitted in fulfillment of Contract EPA 68-02-1331, Task 15, by Lockheed Missiles & Space Company under the sponsorship of the U.S. Environmental Protection Agency. The report covers the period March 30, 1976 to July 16, 1976. Editorial revisions were incorporated in February 1977.

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SECTION 1

INTRODUCTION

SCOPE AND OBJECTIVES

The objective of this task is to evaluate the possible environmental consequences of large scale photovoltaic materials manufacture and to assess potential hazards, relative advantages, environmental control technology requirements, and impact on energy and material resources.

The scope of this task covers silicon (Si), cadmium sulfide (CdS), and gallium arsenide (GaAs) solar cells. The current methods and types of materials and processes are identified in detail. Alternate materials and methods which are being pursued have been identified. Processes, yields, energy, raw materials and waste products are discussed in sufficient detail to estimate quantities.

Primary emphasis is placed on Si for two reasons: (1) the technology is more developed than for the other candidates, and (2) technology growth continues to accelerate (Ref. 1). The principal advantages of the other cell types — low cost of CdS, and high efficiencies of GaAs — have not been sufficiently developed to overcome the low lifetime of CdS and high cost and material quantity limitations for GaAs.

BASIS OF ASSESSMENT

This study addresses the area/mass/efficiency interactions that directly affect raw material quantities, energy, and pollutants generated. The raw material quantities are influenced primarily by three factors:

1. Material in cells: The thickness of the active material in the finished cell from which the ratio of net mass to cell area can be calculated.

2. Production yield: A measure of the amount of material required at the input to obtain the desired amount of material in cells.

$$\text{Overall production yield} = \frac{\text{Amount of active material in solar cells}}{\text{Amount of active material in raw material}} \times 100\%$$

3. Generating efficiency: Several factors influence the efficiency of an installed solar panel. Efficiency is defined as peak power output of the solar cells as a percentage of the incident energy on the solar cell area at solar noon at a location directly under the sun's path at air mass one (AM1) conditions. Local incident energy is affected by latitude, elevation, time of year, time of day, array orientation, weather conditions and local air quality.

Cell output is responsive to energy in the ranges of ultraviolet (UV), visible and near infrared (IR) wavelengths from 0.4 micron to 1.1 micron (Ref. 2). Conversion efficiencies improve with air mass; but, since net incident energy is lower the cell output energy is less. The extraterrestrial solar spectral irradiance value (AM0) of 1353 Wm^{-2} has been determined by extensive tests and standardized (Refs. 3 and 4). The direct solar spectral irradiance at air mass one with attenuation due to atmospheric turbidity, water vapor and ozone is 956 Wm^{-2} (Ref. 5). In addition, there is a diffuse irradiance due to sky radiation which is approximately 20% of the total radiation over all wavelengths. The ratio of diffuse radiation to direct radiation is very high in the UV but drops rapidly in the visible and IR. Solar cells respond to both direct and diffuse irradiance normally. When concentrators are used only the direct component is concentrated.

Efficiency calculations in this study use the peak normal output of cells as a percentage of 1000 Wm^{-2} incident on solar cell area. To determine installed array area required for a specific site, the designer would have to determine local solar incidence, account for packing factor[6], and adjust for structural area, power conditioning, and transmission losses.

Production quantities are based on solar cells providing 1% of the estimated installed electrical generating capacity in the United States in the year 2000. The estimate derived from the Project Independence report (Ref. 6 and others) is shown in Figure 1 to be 900,000 megawatts average. For solar cells to be capable of producing 1% of the generation capacity or 9000 MW average over 24 hours they must have 45,000 MW peak output capability because of the solar insolation curve (see Figure 2). Throughout this report we calculate quantities based on peak output.

Peak Power is the power output of a solar energy system at solar noon directly under the sun's path on a clear day due to direct peak solar radiation at normal incidence. Latitude, time of year and day (solar angle), cloud conditions and local environment are among conditions which affect solar radiation on the solar panel. For simplicity in calculations, peak solar radiation is normally assumed to be 1000 W/m^2.

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[6] Packing factor = solar cell area as percent of total solar array area.

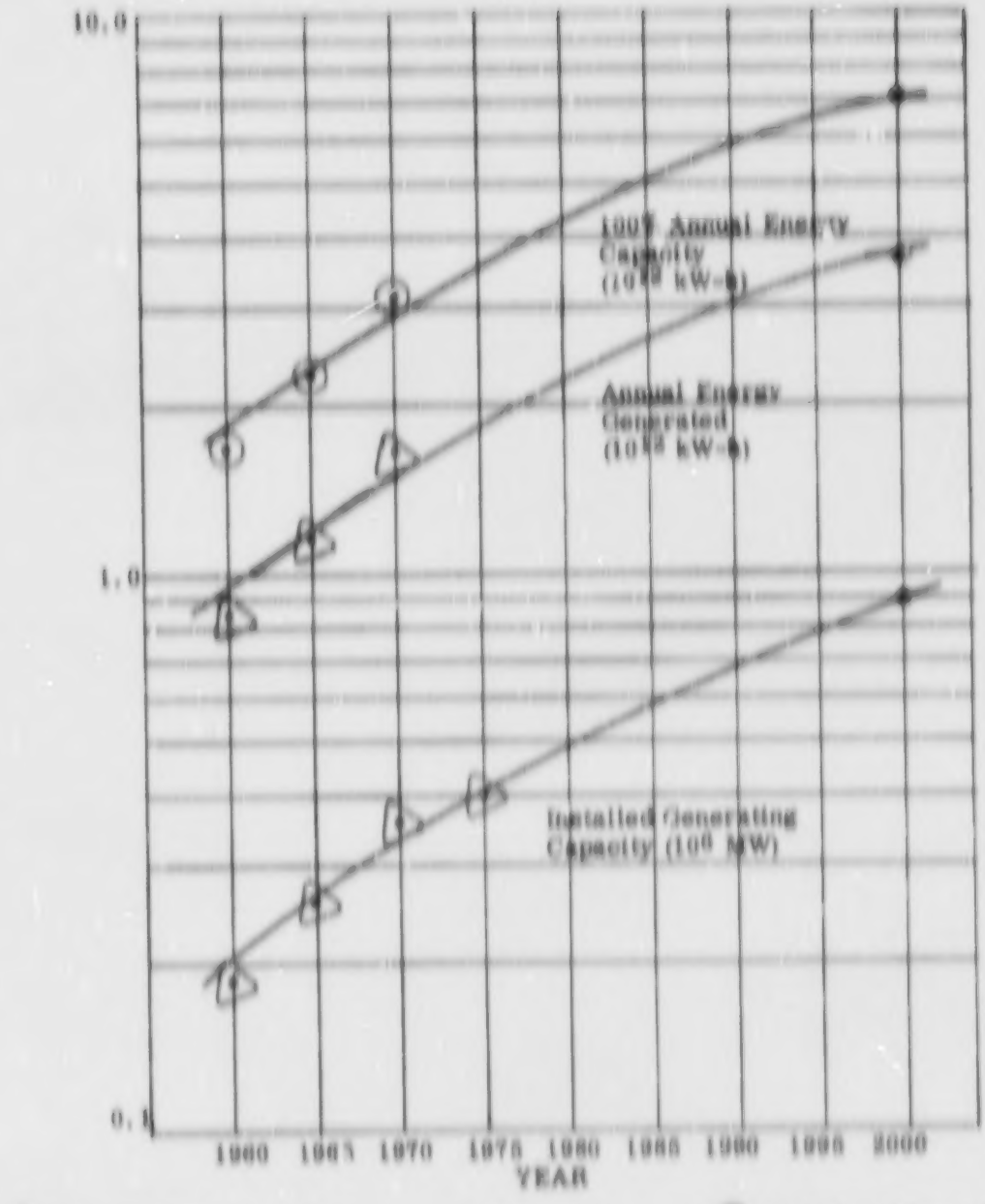


Figure 1. Installed electrical generating capacity in United States.

Average Power is the power integrated over time divided by 24 hours. For this study the ratio of peak to average power is estimated to be 5 to 1 as shown in Figure 2.

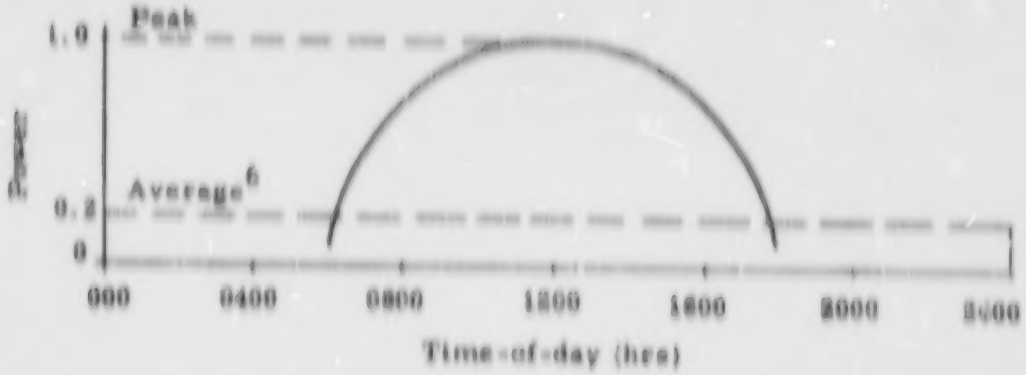


Figure 2. Peak and average solar power vs time for direct radiation on a clear day.

Annual production quantities are based on the best yields, lifetimes, conversion efficiencies and thicknesses for the three cell types which, based on review of published literature, can be achieved currently with little risk. The values used are shown in Table 1.

TABLE 1. SOLAR CELL CHARACTERISTICS AND PRODUCTION REQUIREMENT

Material	Lifetime, Years	Energy Conversion Efficiency, % (Air Mass One)	Thickness, m x 10^{-6}	Annual Production, MW
CdS	5	5	6	9000
Si	10	14	150	4500
GaAs	10	16	125	4500

Note: Annual production is the amount required to maintain a system that produces 9000 MW (average), based on the lifetime of the cells.

The extensive research presently under way in all energy related technologies will cause these numbers to change; therefore the derived data are presented in forms which can be easily factored when performance improvements have been verified.

TECHNOLOGIES EVALUATED

An extensive review of published literature was conducted for each cell type. Conversations with respective leaders in production and analysis of the cell types were conducted to determine the confidence level and probability of fulfilling performance estimates.

Heavy emphasis is placed on silicon and the current ERDA/JPL program (Ref. 7). ERDA programs for alternatives to silicon are being developed and funded. These include GaAs, CdS-Cu_2S and others.

SECTION 4
CONCLUSIONS

SILICON

A major improvement in process efficiency is needed. This should include reduction in the very large power consumption, elimination of the $SiCl_4$ byproduct stream, and reduction in the amount of Si and "SiO" which leaves the plant as solid waste. Although "SiO" is a designated component of several streams, its true identity seems to be questionable in our view, its composition, and implications with respect to plant safety are unclear.

CADMIUM SULFIDE

A very promising process for the production of pure CdS, suitable for solar cells, has been well defined in terms of energy and material balance, pollutants and pollution control technology needs. The techniques for fabricating the laminated solar cells, however, are proprietary and in the early stages of development. Thus, quantitative environmental impact assessment and material and energy balances could not be developed. On a gross, national scale, the atmospheric emission of cadmium or cadmium-bearing particulates is a potentially severe primary pollution problem; discharges of suspended solids, oil and grease effluents are expected to be the most significant secondary pollutants. Adverse local impacts may also exist because of the toxicity of the heavy metal effluents (As, Cd, Cu, Pb, Se and Zn).

The long lead time available before widespread CdS solar cell production occurs (about 15 years), should allow for the development and testing of adequate pollution control technology. The only significant impact on natural resources will be the demand for cadmium, which is a byproduct of zinc production. Demand in the year 2000 from solar cells (36% of the total market) would exert appreciable upward pressures on prices, but demand could probably be met.

GALLIUM ARSENIDE

Many aspects of current and projected GaAs technology remain undefined because of proprietary rights.

Arsenic's environmental toxicity has been reported in research and review literature. By contrast, almost nothing is known about gallium in the environment. Production of GaAs at levels which we have considered in this report will almost certainly create a potential for previously impossible, large-scale environmental releases of gallium.

Current GaAs technology is somewhat energy intensive, but not nearly as much so as Si production.

Gallium may come into short supply unless current hopes for high concentration ratios are realized.

SECTION 3
RECOMMENDATIONS

SILICON

- **Energy Consumption**

Alternative processes which may be less energy intensive need investigation and development.

- **Byproduct and Waste Streams**

Development of a hydrochlorination step to convert $SiCl_4$ to $SiHCl_3$ in a recycle loop needs development and application.

Separation of SiO and Si from the fine particle solid waste stream needs development, so that these may be recycled to the arc furnace and chlorination reactors, respectively.

- **Control Technology**

Fire hazards in dust collector due to purported "SiO" needs to be assessed.

CADMIUM SULFIDE

- **Process Definition**

Further identification and quantification of emissions from the cell fabrication portion of the process is required.

- **Control Technology**

Particulate control device efficiencies for cadmium bearing atmospheric particulates should be assessed.

The adequacy of trace metal removal processes for the control of As, Cd, Cu, Pb, Se and Zn ions in effluent discharges should be determined.

- **Environmental Impact**

After the foregoing are completed, a NEPA EIS on a hypothetical large scale CdS plant is in order to better quantify ecological and other effects.

As part of a comparison of solar versus conventional energy production, a large scale CdS industry should be included in an overall environmental assessment of producing 9000 MW (or more) of electricity by solar versus coal and should include primary and secondary emissions for each.

GALLIUM ARSENIDE

- Gallium in the Environment

Gallium's environmental toxicity and ecological effects must be classified. A definitive literature survey to define future research directions should be the first task.

- Proprietary Information

Feedstocks, chemical intermediates, and plant operations (which currently remains confidential) need identification and characterization.

- Spills

Engineering, regulatory, and management approaches must be developed to minimise risks and consequences of accidental toxic releases.

- Safety

Engineering, regulatory, and management approaches to assure workplace safety must be developed.

- Resource Limitations

The supply/demand picture for gallium needs searching examination.

SECTION 4
SILICON PROCESS

GENERAL PROCESS DESCRIPTION

A process for large-scale manufacture of single crystal Si for solar cells which represents application of current methods is presented in Figure 3. It does not describe any existing facility; however, the technology described is based on Refs. 8, 9 and 10 and the author's projections. Process quantities and operating conditions are based on calculations from handbook data since detailed process information is kept proprietary.

Quartz is reduced by coke in an electric arc furnace to metallurgical grade Si. This process, while requiring high power is approximately 50% efficient. The waste CO stream carries from 15 to 25% of the incoming Si as SiO, which comes off as a light particulate. The SiO is separated and filtered from the gas stream and is conveyed to storage. SiO and Si fines collected from Si milling operations can be used for building insulation, as a filler for lightweight concrete or bricks or they can be compacted and returned to the arc furnace.

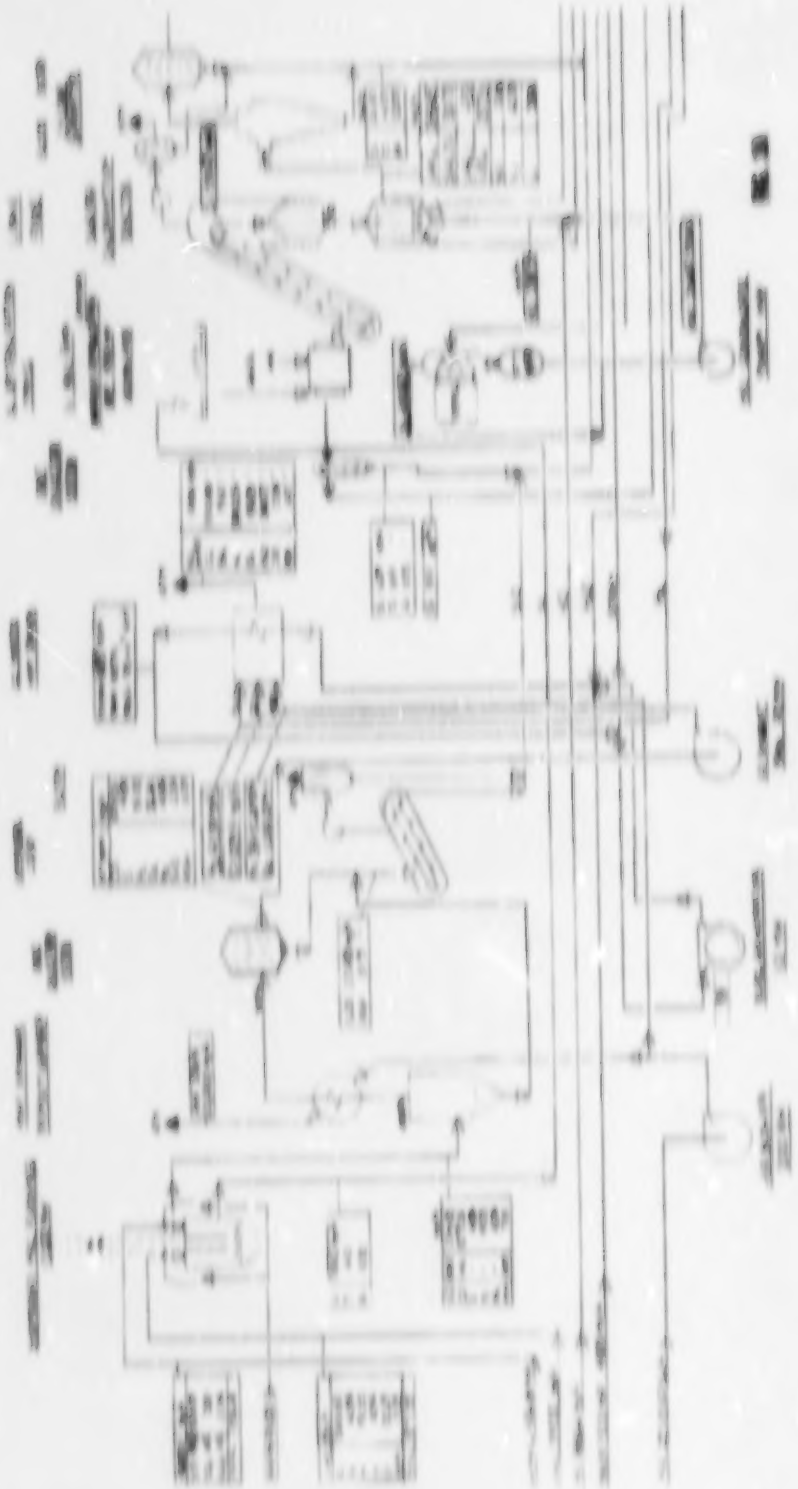
The CO stream, after being filtered of dust, could be used as a fuel, along with waste hydrogen, in a waste heat boiler to produce steam. A small fraction of the steam could be used to heat the silane fractionating column reboiler; the balance could drive a steam generator.

Basic Unit Operations in Silicon Ingot Production

Trichlorosilane--

The metallurgical grade Si is drawn off from the arc furnace in the liquid phase, cooled and allowed to crystallize. It is then milled and fed to a fluid bed reactor and reacted with HCl to produce mono-, di- and trichlorosilane, silicon tetrachloride and hydrogen. A small amount of Si dust is removed from the reactor product stream and then the product gas is run through two sequential condensers to separate a light silane phase, hydrogen and a heavy silane phase. The light silanes, chiefly SiH_2Cl_2 and SiH_3Cl, are recycled to the reactor. The heavier fraction containing trichlorosilane, silicon tetrachloride and dichlorosilane is run through fractioning columns to yield high purity trichlorosilane. The SiH_2Cl_2 with $SiHCl_3$ is recycled to the reactor.

A silicon tetrachloride product is removed to storage for sale, or it may be used for silicon production. Another alternative is to use $SiCl_4$ as



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a starting material for high purity polycrystalline Si; this would give a higher yield of polycrystalline silicon per unit of Si entering the process, but might be more energy intensive. Two producers of polycrystalline Si use the $SiCl_4$ in adjacent silicone plants.

The pure trichlorosilane is fed to a hydrogen saturator where a recirculating hydrogen stream is being saturated with $SiHCl_3$ prior to being fed to the Si rod deposition chambers. In these chambers a thin Si rod is resistance heated to 1370 K where the hydrogen-trichlorosilane to Si deposition takes place. The walls of the deposition chambers are water cooled and the gas stream of approximately 95% hydrogen is purified, resaturated with $SiHCl_3$ and recirculated through the chambers several times. A near-turbulent gas flow is desired with a resultant deposition rate of approximately 10 μ/min. This slow rate (1.44 cm/day) demands three to four days to grow a common ingot and consequently this one step is more energy intensive than all else combined. A fair quantity of cooling water is required, however, it can be recirculated through a cooling water tower thereby requiring only makeup water to replace evaporative losses.

Silicon Rod Deposition--

The hydrogen-rich exit stream from the Si rod deposition chambers carries a mixture of silanes, silicon chlorides, hydrogen-chloride and hydrogen. Sequential condensers separate and return these products to the process for recycling. No silanes, silicon chlorides or HCl are vented to atmosphere at any time. A slight excess of hydrogen gas is produced and burned in the CO waste heat boiler.

The major potential pollution problem is dust. The following operations will require some form of dust control.

Coke and Quartz to the Arc Furnace--

Coke in briquet form and quartz in chunk form would be transported by rail or truck to the plant site and by belt or bucket conveyor to the furnace. Closed bulk handling equipment may be required; however, the particulates are expected to be large at this stage and may not require special consideration.

SiO and Ash from the CO Stream--

The CO stream carries fine SiO dust with it. The particle size distribution of this dust was unavailable at this writing; therefore it was estimated that a high-quality dust collection system would trap 99 percent of the solids. The remaining fine dust would go through the waste heat boiler stack either to additional dust precipitation equipment or, if concentrations are low enough, to the atmosphere.

Milling and Conveying of Metallurgical Silicon--

Further investigation is necessary to ascertain the fineness of the milling required for the fluid bed reactor. Nevertheless, there will be some fine silicon dust generated which will require enclosure of the mill and exhaust air filtration.

Boiler Flue Gases--

The exhaust stack from the CO waste heat boiler will contain a small concentration of SO_2 if high grade coke is used in the arc furnace. If the coke has a high sulfur content it could become necessary to use a scrubber on the stack. Some oxides of nitrogen may also be expected in the waste heat boiler stack gases. A small quantity of nitrogen enters the process stream with the coke and is expected to remain in the CO gas stream to the waste heat boiler where oxides of nitrogen can form. The operating conditions of the boiler affect NO_x generation and gas composition.

Crystal Doping--

The solar-grade polycrystalline Si proceeds to cell fabrication where it is transformed into one of the forms of cells noted in Table 2. The polycrystalline material must be doped to form either p-type material (boron, etc.) or n-type material (phosphorous, etc.). The amount of dopant is determined by the desired bulk resistivity. A target resistivity for silicon of 0.25 ohm-cm requires 3×10^{16} atoms/cm^3 of n-type dopant (As, P, Sb); or 1.2×10^{17} atoms/cm^3 of p-type dopant (Al, B, Ga) (Ref. 11).

TABLE 2. PROPOSED CELL TYPES (REF. 7)

Single crystal	
	Wafers sliced from crystal
	Sheet grown crystal -- by EFG[9] or other
	Epitaxially grown crystal on substrate
Polycrystalline	
	Chemical vapor deposition (CVD)
	Zone crystallized sheet

[9]Edge-fed film growth.

If all of the polycrystalline Si is doped with boron to form p-type material for N on P solar cells the amount of boron required is 1.49 gm/MW of peak array output. This equates to approximately 20 milligrams per hour in a facility which produces 100 MW/yr. For n-type material (for P or N

solar cells), 4.47 gm of phosphorus per megawatt (approximately 50 milligrams of phosphorus per hour for a 100 MW/yr facility) are required. The dopant is added to the polycrystalline melt prior to single crystal growth. For this study boron doped material is used for the bulk cell wafer. N or P denotes n-type or p-type material.

Crystal Growth--

Single crystal silicon ingots for solar cell fabrication are grown in sizes ranging from 5 cm to 15 cm diameter, weighing from 9 to 36 kg each.

The polycrystalline Si and dopant charge are placed in a quartz crucible which, in turn, is placed into an electrically heated carbon bowl. Agitation of the melt assures uniform dispersal of dopant and proper crystal orientation during growth is accomplished in an atmosphere of high purity argon.

A seed crystal of Si is introduced to the melt to form the crystallization nucleus. It is slowly drawn from the melt as the crystal forms. Constant monitoring of controls by a trained operator is required to ensure good crystal yield. The operator must adjust controls in response to variations in the crystal growth parameters. At present one operator is required for two to four crystal growing machines.

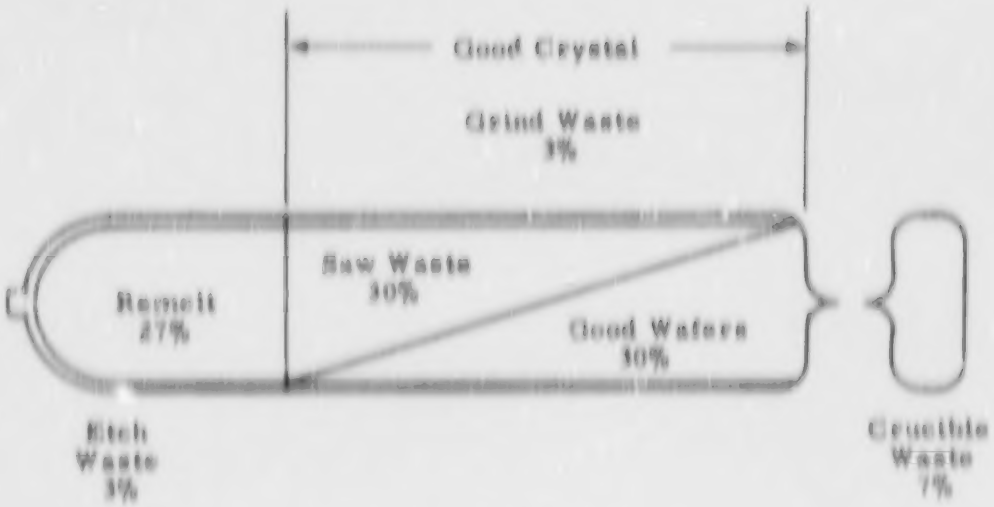
The resultant crystal is approximately 90% of the polycrystalline Si. The remaining 10% is crucible waste. It, along with the crucible itself, could be recycled to the arc furnace to provide some cost savings. Figure 4a shows the utilization of the ingot. Thirty percent is high purity Si which is not suitable for producing cells but it is remelted for crystal growth after etching away its oxide coating. Figure 4b shows the current net yield of polycrystalline Si into wafers for cell production.

Cell Fabrication Sequence

Cell fabrication for this study is based on Czochralski grown single crystal Si which is sliced into wafers. Process flow is diagrammed in Figures 5 and 6. Currently, sliced single crystal technology has several advantages over other methods of cell production. It is well known, proven, and has near term growth potential (Ref. 12) to produce more kilowatts/kilogram of Si (because of higher material utilization and higher cell efficiencies).

Wafer Slicing--

The two most popular methods for wafer slicing are: (1) cutting single slices with diamond blade, and (2) multiblade slicing with abrasive slurry. Of these the multiblade slicing is the most promising for both high production and minimum wafer damage. It is less sensitive to diameter than the diamond blade and can accommodate multiple ingots with some modification. The apparent limitations with diamond blade cutting are that with increasing



a. Single Pull

Other Waste 23.4%	Saw Waste 36.3%	Wafers 40.3%

b. Net Yield Assuming Remelt Recycled Twice

Figure 4. Current silicon yields as percent of polysilicon input to crystal growers.

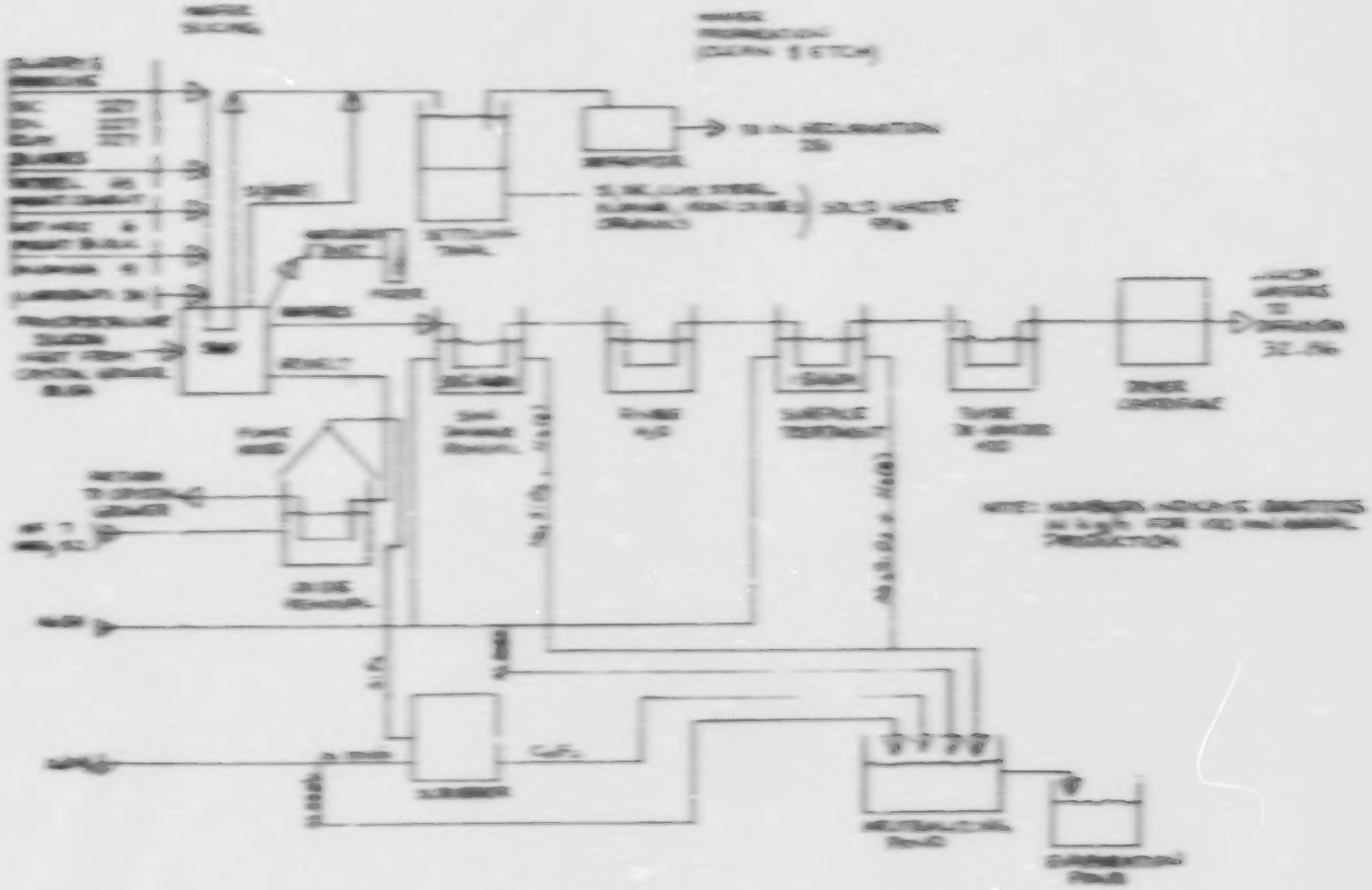


Figure 5. Silicon cell fabrication flow diagram – wafer preparation

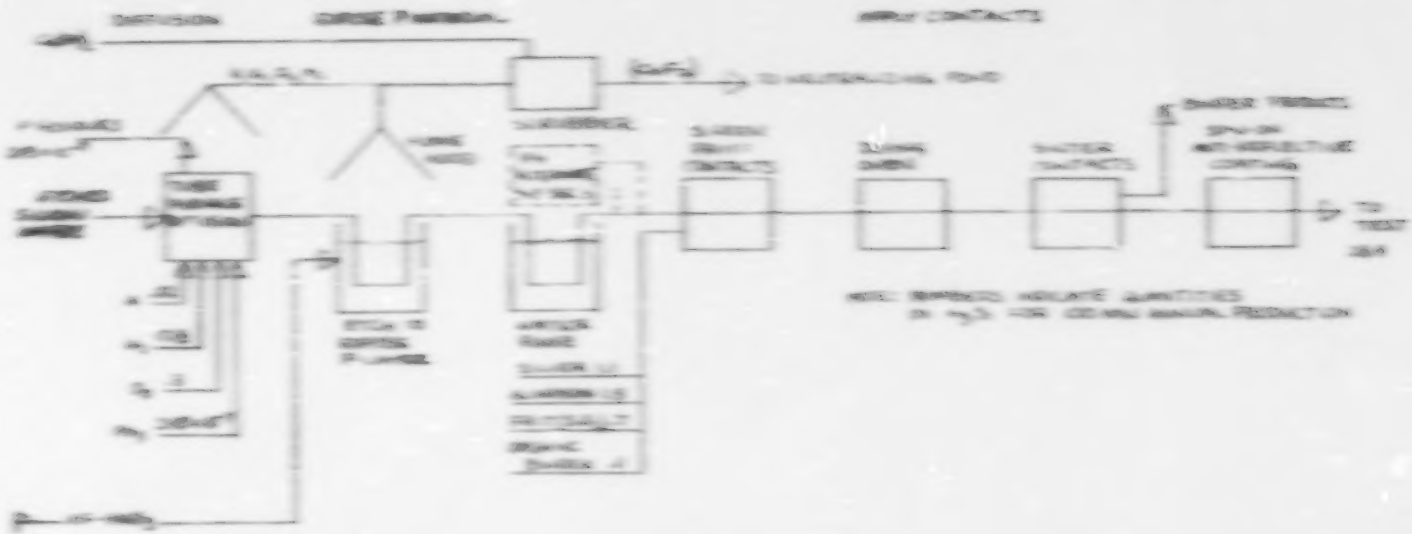


Figure 6. Silicon cell fabrication flow diagram – diffusion to electrical test.

ingot diameter: (1) the blade causes chatter damage to the wafer, and (2) the blade must be thicker causing more kerf loss and reduced material utilization.

Of the 60% of the polycrystalline entering the melt which becomes single crystal Si and is suitable for producing solar cells, half is removed as saw kerf. This material has large surface area which oxidizes readily. It also is contaminated with SiC grit used in cutting and ceramic from the blocks used to support the ingot during cutting.

Programs to reduce the saw kerf and improve surface finish as well as to reduce wafer thickness which can be cut are being performed under ERDA-JPL contracts (see Ref. 7).

The single crystal ingot is sliced to the maximum length that the machine can accommodate and bonded to a ceramic submount with hot melt adhesive or wax. The submount is either alumina or other material which has about the same density and cutting qualities as Si. The submount must be thick enough to permit the blade to cut half of its depth into the submount to assure that no tapers remain on the wafers. 0.5 kg of alumina per kilogram of polysilicon is required. The amount of adhesive or wax is estimated to be 0.07 kg per kilogram of polysilicon.

The cutting results from the abrasive action of steel bands rubbing grit on the Si. The highly-tensioned and accurately-spaced steel bands are pressed against the Si and drawn across in a reciprocating motion while the abrasive slurry is fed to the bands. The abrasive slurry consists of: (1) the Si carbide abrasive (usually 600 mesh), and (2) the slurry vehicle which is an oil base mixture with fine clay which holds the grit in suspension. The slurry vehicle most commonly used has a flash point of 275 to 300 F and is noted as a non-hazardous material for shipping.

The required amount of slurry is 8.3 kg per kilogram of polycrystalline Si. If equal parts of oil, clay and grit in the slurry are assumed then there will be 2.77 kg of each per kilogram of polycrystalline silicon. Present equipment recirculates 99% of the slurry, leaving 1% which may become airborne in the cutting area. Control of the 1% may be required to prevent inhalation by personnel.

Other consumables during wafer slicing are the blade pack and lubricants. The blade pack consists of 10 mm thick strips of steel 0.1 mm wide spaced 0.15 mm apart. Each pack is estimated to last 10 cuttings. Therefore the steel consumption during cutting is approximately 0.77 kg per kilogram of polycrystalline Si.

Air/oil mist lubrication is used for the guide mechanism. This mist is sprayed on the bearing cages of the four guide shafts. Most of the mist is trapped and drains into an open collection trough in the cutting machine. Some of the mist becomes airborne in the area around the machine. A rough estimate for the quantity consumed is 0.3 kg lubricant/kg polycrystalline Si with 5% becoming airborne. Cutting energy is estimated to be 7.5 kWh/kg

of polycrystalline Si. For this study 40.1% of the polycrystalline Si is assumed to emerge as wafers for cell processing.

Wafer Etching (Ref. 13)--

The wafers from the saw have mechanical damage resulting from the 600 grit abrasive which is approximately 15 μm deep. To remove this damage 15 to 25 μ of wafer is etched away in heated 30% by weight NaOH. An additional 15 to 25 μ of wafer is removed in a 1% NaOH solution. This second etching produces a rough surface which has low reflectance and improved adherence of metallization.

The reaction taking place in the sodium hydroxide etching is:

$$Si + 2\ NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2$$

Each kilogram of polycrystalline Si produces approximately one square meter of wafers and the above reaction must remove 15 μ from each side of the wafer. On this basis it is estimated that 20 gm of NaOH are required per kilogram of polycrystalline Si. These estimates are based on stoichiometric reaction -- the efficiencies of the etching processes are unknown to the authors. Thirty-one grams of Na_2SiO_3 are produced during each etch in addition to 4 gm of hydrogen. Following the etch the wafers are rinsed with deionized water and dried to prepare them for the diffusion process which follows.

Diffusion Junction Formation (Ref. 14)--

A layer of n-doped material is formed on the wafer by diffusing phosphorus into the crystal structure in a tube furnace. To quantify the potential pollutants a description of the open-tube phosphorus diffusion process which uses a phosphine (PH_3) gas source is required. A gas mixture of 1% PH_3 and 99% argon, with some further dilution nitrogen, is fed to the tube furnace where the PH_3 is dissociated.

$$2\ PH_3 \xrightarrow{713\ K_{+}} 3\ H_2 + 2P$$

Oxygen is provided to produce phosphorus pentoxide.

$$4\ P + 5O_2 \longrightarrow 2\ P_2O_5$$

As the P_2O_5 strikes the surface of the wafer it reacts to form a glassy layer by this reaction:

$$2\ P_2O_5 + 5\ Si \longrightarrow 4P + 5\ SiO_2$$

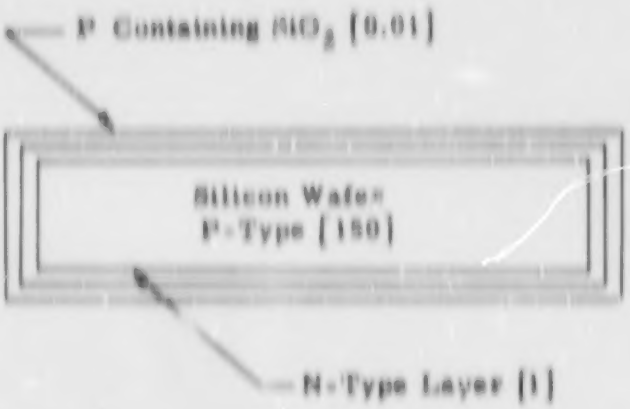
The portion of the phosphorus in this layer which diffuses into the Si determines the electrical property of the junction.

The Si wafer already contains 1.2×10^{17} atoms of boron/cm^3. To achieve the desired net density of doping of 1×10^{16} atoms of phosphorus requires a total of 15×10^{16} atoms/cm^3 in the layer. The quantity of dopant in the layer can be calculated. There are 6.2×10^{-6} g of phosphorus in the layer, per square meter of wafer area. To achieve this level of doping requires 3×10^{-6} kg of PH_3, 180 cm^3 of argon, 190,000 cm^3 of nitrogen and 2700 cm^3 of oxygen per kg of polycrystalline Si.

At the exit from the furnace the excess phosphorus reacts with air to form a mixture of P, P_2O_5 and H_3PO_4. The disposal or recovery of these products may include recycling PH_3. Because of the toxicity of PH_3 and related compounds, a negative pressure gradient must be maintained between the inlet (where personnel load the furnace) and the exhaust from the tube furnace. This is an occupational safety and health problem, but not an environmental problem. Diffusion process energy requirements are estimated to be 18.6 kWh/kg of polycrystalline Si.

Exposed Material--

The diffusion process leaves the wafer coated with an n-layer and an outer surface of SiO_2 which contains phosphorus as shown in Figure 7. SiO_2 must be removed from both sides of the wafer and the n-layer from



[ ] = Thickness (10^{-6} m)

Figure 7. Silicon wafer cross-section after diffusion.

one side to expose the P material. This is accomplished with an acid etch as follows:

$$4\,HF + SiO_2 = SiF_4 + 2H_2O$$

$$4\,HNO_3 + 5\,Si = 5\,SiO_2 + 2N_2 + 2H_2O$$

The resulting SiF_4 gas may be scrubbed with $Ca(OH)_2$ to form CaF_2 which is relatively insoluble in water.

To remove one micron of Si requires 6.33 gm of HF and 4.2 gm of HNO_3/kg of polycrystalline Si, assuming 1 m^2/kg of polycrystalline. There are 8.5 gm of gaseous SiF_4 to be scrubbed per kilogram of polycrystalline.

Reclamation of Silicon Ingot for Remelt--

As noted above, part of the Si ingot is unsuitable for slicing into wafers but is capable of being remelted at the crystal puller after the oxide layer is removed. HF-HNO_3 is used to remove the outer 10% of the ingot prior to remelting. This reaction requires 0.08 kg of HF and 0.06 kg of HNO_3 and produces 0.11 kg of SiF_4/kg of polycrystalline Si.

Apply Contacts--

Screen printed contacts have been shown to be suitable for terrestrial solar arrays and for high production (Ref. 13). The composition of these contacts is proprietary but they are known to contain silver, aluminum, silica and an organic binder. For this study we have assumed the relative volume composition to be 10% silver, 50% aluminum, 30% silica, and 10% binder. Assuming 75% yield of 8 μ thickness and 14% front coverage and 95% back coverage, the amount of contact material is 11.63 cm^3/kg of polycrystalline Si. Quantities of each constituent per kilogram of Si are aluminum, 16 g; silver, 13 g; SiO_2, 9g; and binder, 1 g.

Firing Contacts--

After the screen printed contacts are thoroughly dried they are fired at approximately 923 K to sinter and drive off the binder. The products of the binder will have to be determined and their environmental effects assessed. Estimated energy is 7.6 kWh per kg of polycrystalline Si.

Anti-Reflective Coating--

Si covered cells made with the NaOH etch process showed a 2% drop in output when compared with silicon covered cells with spin-on and vapor deposited anti-reflective coatings (Ref. 15).

The spin-on process is used because it does not require a vacuum. An 0.1 μ coating of TiO_2 and SiO_2 is spun onto the front of the cell and sintered at 523 K. This requires approximately 2.7 g each of TiO_2 and

SiO_2 (assuming 10% deposited on the cells) and 10 kWh of electrical energy per kg of polycrystalline Si.

Electrical Test--

The final step in cell production is the electrical test under a solar simulator. Environmental and personnel safety aspects of the test include high voltages and UV radiation. Presently tests are conducted at low levels, but increased production would demand more detailed study to ensure personnel safety.

Cell Processing Yield

This study assumes a cell processing yield from wafer to finished cell of 85%. The net yield based on polycrystalline Si to finished cell is 34.8%.

Material Consumption and Production Estimates

Material Utilization--

When cell wafers are cut from an ingot such as in the current Czochralski crystal growth and slice method, the maximum material utilization is limited by the saw kerf and wafer damage during sawing. During slicing by either the internal diameter diamond saw with its 5 to 10 mil kerf or the multiple band slurry saw with its 4 to 10 mil kerf, there is some damage to the wafers that must be etched away or otherwise treated. With further development of the sawing method, the potential is for 0.10 mm wafers with 0.10 mm kerf with no wafer damage (Ref. 16) which is the utilization limit for sliced wafers. There is no possibility of increasing area by reducing wafer thickness because thinner wafers become too fragile for the slicing operation. If thinner wafers are desired they are chemically etched from 0.1 mm wafers. Thus the maximum area that can be produced from sliced material is 2.1 m^2/kg of net Si which corresponds to 0.10 mm (or thinner) wafers with 0.10 mm saw kerf. This study assumes 0.15 mm thick wafers with 0.15 mm of saw kerf, which when combined with yield factors, produces 1 m^2/kg of polycrystalline Si. Other methods of utilizing Si (e.g., vapor deposition in 10 μ thickness) may permit an order of magnitude increase in area to mass ratio. However, cell collection efficiency is reduced rapidly when base diffusion lengths are less than 0.015 mm (Refs. 17 and 18).

Production Yield -- Czochralski--

The production of single crystal Si for solar cells involves the melting of polycrystalline high purity Si with a suitable dopant and the growing of the single crystal by introducing a "seed" crystal. The temperature, atmosphere, agitation and rate of pull are carefully controlled during crystal growth to maintain a properly oriented single crystal. The net yield of wafers from the saw is 40.1% of the polycrystalline Si supplied to the crystal grower.

Of the wafers entering the cell production line, 60 to 90% will emerge as completed electrical cells. Eighty-five percent is projected as 1977 capability (Ref. 13) and is used for this study.

Polycrystalline Si Requirements--

The estimated 14% electrical conversion efficiency will result in 140 watts per square meter of 150 μm thick finished cells. This is equivalent to 0.40 kW/kg of Si in finished cells or 0.14 kW/kg of polycrystalline Si (using 34.8% yield of cells from polycrystalline silicon).

The quantity of polycrystalline Si required to produce 4500 MW (peak) annually is, therefore, 32.14×10^6 kg. (This will produce 11.2×10^6 kg of finished cells). The quantity used (as discussed earlier) is 81.54 kg/hr for a plant which produces 100 MW/yr. Based on the polycrystalline Si requirement, other material requirements for the above solar cell production were estimated and are listed in Table 1.

Silicon Byproducts--

SiO and Si fine particulates are low density, excellent insulating materials. Fine silica particles are presently being sold for high quality thermal insulation. This material could also be used as lightweight filler in concrete or bricks.

The "$SiCl_4$" stream has the following composition:

Substance	kg/h	%
$SiCl_4$	1226.41	63.1
$SiCl_2$	714.57	36.8
$SiCl_3$	1.84	0.1
Total	1942.82	

or 17×10^3 metric tons annually. $SiCl_4$ is much too valuable to be treated as a waste stream, even were this environmentally acceptable. Consequently, a Si tetrachloride product is removed to storage for eventual sale. It has a market price of approximately 13 cents/kg. It can be used in Si production or as a starting material for polycrystalline Si production by a different process. This would give a higher yield of polycrystalline Si per unit of Si entering the process, but might be more energy intensive. Two producers of polycrystalline Si use the $SiCl_4$ in adjacent Si plants. $SiCl_2$ is a major constituent of the "$SiCl_4$" byproduct stream. We have not investigated its effect upon the marketability of $SiCl_4$.

Methods of hydrogenation of $SiCl_4$ and $SiCl_3$ should be investigated. It may be economically advantageous to include within the plant an $SiCl_4/SiCl_2$ recycle loop through a hydrogenation facility which converts chlorides to chlorosilanes, particularly $SiHCl_3$.

For the latter conversion, the reaction

$$SiCl_4(g) + HCl(g) \rightarrow SiHCl_3(g) + Cl_2(g)$$

TABLE 1. MATERIALS AND PRODUCTS FOR 4500 MW ANNUAL SILICON CELL PRODUCTION (10^5 METRIC TONS)*

Solids	Quantity	Solids	Quantity
Quartz, 98% SiO_2	6.13	Solar Cells	0.11
Coke, 92% C	2.36	Si	0.12
Boron	8×10^{-8}	Si Carbide	0.89
Si Carbide	0.89	Clay	0.89
Clay	0.89	Steel	0.26
Steel	0.26	Adhesives	0.02
Adhesives	0.02	Alumina	0.16
Alumina	0.16	CaF_2	As req'd
$Ca(OH)_2$	As req'd	Phosphorus residues	9.6×10^{-10}
Aluminum	0.005		
Silver	0.004		
SiO_2-TiO_2	0.003		
Liquids		**Liquids**	
HCl 99.9%	7.37	$SiCl_4$	4.83
		$SiCl_3$	7.25×10^{-3}
		$SiCl_2$	2.82
		Oil	0.89
Oil	0.89	Lubricant	0.09
Lubricant	0.09	Na_2SiO_3	0.02
Gases		**Gases**	
Air	108.06	CO_2	7.92
Argon	0.35	SO_2	0.04
Nitrogen	0.07	NO	0.04
Oxygen	0.001	H_2O**	1.34
PH_3	9.6×10^{-10}	Ar	0.35
		H_2	Trace
		Fine Particulates (Airborne and Solid Waste)	
		SiO	0.87
		Si	0.17
		Ti	0.02
		Al	0.05
		Ash	0.04
		Aerosol (oil and lubricant)	Trace

*To convert from test data (kg/h for 100 MW production) to units of this table (10^5 MT/yr for 4500 MW production) multiply by 3.94×10^{-3}.

**Does not include boiler feed or cooling water.

has an endothermic heat of reaction

$$\Delta H^{298^{\circ}} = 61.8 \text{ kcal/mole} \quad \text{(Ref. 19)}$$

which is not prohibitive. High temperature equilibrium partial pressures for most of the Si chlorides and chlorosilanes, H_2, HCl, and monatomic Cl have been reported in a paper by Sirtl et al. and by references quoted therein (Ref. 19).

Were the Si chloride "byproduct" stream 100% converted to $SiHCl_3$, an immediate 59% increase in polycrystalline Si production would result. Looked at another way, this would result in a 37% reduction in mass of pollutant released per ton of product or megawatt of power consumption at the submerged arc furnace. From the vantage point of plant management, this would make for easier compliance with current New Source Performance Standards (NSPS) for particulate emissions. Plant performance with regard to NSPS is discussed in a later section.

Plant Siting

The preceding discussion does not imply that the entire production train — from quartzite to finished solar cells — necessarily will be located inside one plant or that all plants will even be in the same region of the U.S. First plants (if of new design) possibly will be located on the basis of Federal funding for demonstration plants and other forms of institutionalized seed money. Subsequent facilities are more likely to be financed privately. Siting may be near raw material, near cheaper hydropower, by product recovery plants, near product market, or added on to existing ferrosilicon production facilities.

Single crystal ingot production from quartzite and coke naturally falls into three process segments, which may be remotely located (cf., Figure 3):

- Crushed Si metal production terminating at the 5 kW Si mill. This segment is most likely to be located in urban industrial areas in regions near metallurgical coking coal, or abundant quality quartzite.
- Pure polycrystalline Si production beginning with the fluid bed chlorinator and ending with the 1 kW rod crusher. This segment would find Si elastomer industry and cheap hydropower attractive.
- Single crystal ingot production, namely the 5 MW pulling chamber. This third segment is most likely to be located near existing electronic industry.

POWER REQUIREMENTS

The estimated power requirements for the manufacture of Si solar cells, discussed earlier, are summarized in Table 4. Power rather than energy is used for two reasons: (1) the processes lend themselves to continuous operation, and (2) a direct comparison to solar cell output can be

TABLE 4. SUMMARY OF POWER REQUIREMENTS FOR ANNUAL PRODUCTION OF 4500 MW OF SILICON SOLAR CELLS

Equipment or Operation	Power, MW
Arc Furnace	765.00
SiO Conveyor	0.05
CO Exhaust Fan	0.90
CO Waste Heat Boiler Steam Generator	-45.00
Air Blower	9.00
Si Mill and Conveyor	0.25
HCl Condenser-Refrigeration	45.00
HCl Condensate Pump	0.05
Silane Condensate Pump	0.09
Refrigeration for Light Silanes Condenser	2.25
Silane Bottoms Pump	0.09
$SiCl_4$ Pump	0.09
$SiHCl_3$ Pump	0.09
Condenser-Refrigeration for Silanes from Deposition Chambers	22.50
Si Deposition Recirculation Blower	0.90
Si Rod Deposit Chambers	3,240.00
Si Rod Crusher	0.05
Cooling Tower Water	45.00
Crystal Growth	255.00
Slice Wafers	27.50
Diffuse Wafers	68.50
A/R Coating and Sinter	36.70
Firing Contacts	27.90
Test	55.00
Miscellaneous Waste Handling and Environmental Controls	20.00
Total	4,574.35

made. The power estimates are for cell production only and do not include allowances for coverglass, electrical interconnects, solar array mounting structure, power conditioning, manufacturing facility utilities or energy residuals (cf., the following section). However, these factors are expected to be only a small fraction of the process power defined.

The 4500 MW of solar cells represents peak power, peak sun exposure, or average power over 24 hours of 900 MW. Power payback on silicon solar cells is then calculated as follows:

$$\frac{4574.35 \text{ MW to produce cells}}{900 \text{ MW/year from cells produced}} = 5.08 \text{ years}$$

Before conclusions are drawn a number of factors should be taken into consideration as follows: (1) the process described and power consumed are based on simply factoring up present small-scale production,

and (2) new technology will replace or improve present processes. Current efforts under ERDA-JPL (Ref. 7) are directed toward that end. As Table 4 shows, the rod deposition of Si from $SiHCl_3$ consumes 70% of the electrical power requirement; any improvement in this process or its replacement by a less energy-intensive process offers a large incentive. As discussed earlier, a saving in power (exclusive of deposition and pulling chambers) can be made by conversion of the Si chlorides byproduct stream to $SiHCl_3$.

Energy Residuals

Two major raw materials, quartz and coal, are open-pit mined. Coke is used in the arc furnace reduction of silica and therefore, there is a requirement for mining approximately 1/2 kg coal per kilogram of Si. Comparable quantities of coal as fuel for energy generation versus required quartz and coal to make solar cells is calculated using the following assumptions:

1. Coal to coke conversion of 70%
2. Coal to electrical conversion of 30%
3. Ten year cell life at average power 20% of peak power.

The 100 MW of electrical power generated by the solar cells produced annually in one hypothetical plant yields 1.752×10^9 kWh over a ten year life. These solar cells require 15.36×10^6 kg of quartz and 6.87×10^6 kg of coal to be mined. To produce an equivalent amount of energy from burning coal requires the mining of 9.08×10^8 kg of coal. Thus, the production of solar cells requires mining only 1/45 the material consumed by coal-fired power plants.

The direct and indirect environmental problems of silicon cell manufacturing process are discussed in the following section.

Energy Payback and "Ungenerated" Pollution

The amount of pollutants "saved" by the use of solar cells as compared to coal-fired or other electrical power generation is proportional to the amount of material mined and burned or reacted.

During initial production, there is an investment of the "dirty" energy required to produce the first solar cells. Using an energy payback period of five years and a lifetime of 10 years we obtain a 2 to 1 energy advantage.

ENVIRONMENTAL CONSIDERATIONS

For purposes of assessing its environmental effects, Si differs from cadmium sulfide and gallium arsenide photovoltaic material in three important ways:

- The principal substance is itself non-toxic;
- its production consumes large amounts of energy;

- its principal raw materials must be mined and processed. For their own value in Si production – they are not byproduct minerals arising from extraction of a more valuable resource.

SiO_2 (Silica) Mining (Refs. 20 and 21)

About 94.8 kg of 98% silica are required for every kilogram of solar cell Si ultimately produced.

Quartzite mining problems are similar to those for other low-value materials, namely, trying to obtain maximum output at the lowest possible cost. The mining of quartzite presents a unique problem due to the abrasive nature of this material, which causes excessive wear on drilling and processing equipment. The toxic nature of Si dust is another problem which requires constant attention to hygiene in both mining and processing operations (Ref. 22).

The silica raw materials in demand for production of Si and ferrosilicon – lump quartz, quartzite, or well-cemented sandstone – should contain 98% or more silica. Preferred size is between 2 and 15 cm, with quartz pebbles generally acceptable as small as 1 cm. Because of the violence in the furnace and high volumes of waste product, large chunks of silica raw material are preferred, although quartz sand and gravel have been used at some plants.

Mining of silica is confined to surface operations. Conventional equipment such as bulldozers, power shovels, loaders and haulage trucks are used. After overburden is removed the exposed silica is removed by draglines and/or power shovels and washed and crushed. Quartzite and well-cemented sandstone require blasting with wagon drills commonly used for the primary drilling and ammonium nitrate-fuel oil mixtures used for blasting.

High grade quartzite needs only crushing and sizing to prepare it for the smelting furnace. The price of 99% pure quartzite produced in the Oro Grande district of California has been estimated at approximately $6/ton plus an additional freight cost of $2 to $3/ton to deliver it to the smelting furnace. One of the smaller quartzite mining operations which uses blasting and size reduction reported a productivity figure of approximately 3 tons/manhour. This did not include processing or overhead.

The most obvious environmental impacts of open pit silica (quartzite) mining are:

- Irretrievable Land Use Commitment
- Fugitive Dust
- Noise
- Indirect Socio-Economic Effects.

Although locally significant, nationwide the amount of land disturbed in mining silica raw materials for Si production is insignificant when compared

with the mining of silica sand and gravel for construction and other uses. Sand and gravel mined approximates 1×10^9 MT annually, while current requirements for Si metal for all uses is estimated at less than 0.7×10^6 MT.

Projected demand in the year 2000, without regard for solar applications, is about 3.5×10^9 MT sand and gravel and 1.6×10^6 MT metallic Si. To supply Si solar cell fabrication needs at the rate of 4500 MW equivalence annually would require an additional 0.6×10^6 MT Si. The total, 2.2×10^6 MT, corrected to SiO_2, represents 0.13% of sand and gravel demand for year 2000 (Refs. 20 and 21).

All quartzite mining is by the open pit method, and the overburden to ore ratio is nominal. Thus, the proliferating spoil heaps characteristic of coal mining are a relatively insignificant, and tractable, problem in quartzite mining.

Fugitive dust emissions at quartzite mines arise mostly from loading and movement of trucks, from drilling, and from crushing. In fact, unpaved roads represent 90% of all fugitive particulate emissions in the U.S. Chatekode and Blackwood (Ref. 23) measured emission factors for various unit operations in the quartzite mining, and reported average trace element concentrations for suspended particulate in open quartzite mines. Their data (translated to metric ton solar cell equivalent) are shown in Tables A-1 and A-2. Average free silica content of dust from unpaved quartzite mine roads in the U.S. was 17% (weight) with a 95% confidence interval of ±11%. The corresponding threshold limit value (TLV) for this mine road dust would be 1.5 mg/m^3. The authors report that no dust control measures were observed at quartzite mining sites. Wet drilling, drill bit collars, and wet or oil sprays on haul roads are control measures applied successfully at granite, taprock, and limestone plants. These measures seem applicable also to quartzite mining.

Even without control measures, quartzite mining does not seem to be a major dust and particulate source ascribable to solar cell manufacture. In fact, we will see in the next section that it is trivial relative to the impact of metallurgical coke production.

Effluent limitations guidelines for industrial sand and gravel mining and processing have been promulgated (Ref. 24) but none exist for quarrying. The "Best practicable control technology currently available" (BPCTCA) degree of effluent reduction limitations applicable are:

- TSS: 30 mg/ℓ
- pH: 6.0 to 9.0.

These are not translatable into pollutant release per unit mass of resource. In any event, quarried lump quartzite is preferred to sand, as discussed earlier.

"Noise pollution" is dependent on plant geography, topography and size, for example subsurface hydrologic modifications can result if a quartzite

caprock is removed from its underlying limestone. Surface drainage is effected by removal of sand and gravel deposits. These effects are however, wholly site specific.

Coke

The discussion that follows is intended to orient the reader to some of the literature describing current problems in coke production, and to present a "worst case" estimate of atmospheric emissions in coke production. A detailed discussion of water and air quality problems and environmental pollution control in the manufacture of metallurgical coke is beyond the scope of this report.

High grade metallurgical coke is used for reduction of SiO_2 (quartz) in the arc furnace. For each kilogram of Si in the solar cells ultimately produced, about 3.1 kg coke is required. This may correspond to as much as 10 kg coking coal, depending on the design of coke batteries used. The equivalent energy consumption was discussed earlier.

Although briquetted or lump coke is used as arc furnace feedstock, routine materials handling will generate some coke dust. Simple hooding (Ref. 25) with exhaust air filtration seems appropriate in problem areas.

Vastly more significant environmental problems result from coke oven operation and coke quenching.

All of these are subjects of a voluminous literature. Coke oven operation and coke quenching technology (Ref. 26) are changing rapidly. Many coke plants are very old. Nineteenth century "beehives" (Ref. 27) are still in operation, for example. Nevertheless, we expect that by 1982 45%, and by 2000 most of the oldest plants will have been scrapped and replaced (Ref. 28) with modern facilities employing sealed push and hooded techniques (Ref. 29) or even dry quench (Ref. 30). Also, conventional byproduct coking may be increasingly displaced by "formed coke" processes (Ref. 31) capable of utilizing marginal or lower grade coking coals in a closed system and by continuous and pipeline coke, also capable of closed system operation (Ref. 32).

Both USEPA and the U.S. Labor Department's Occupational Safety and Health Administration (OSHA) have jurisdiction over atmospheric emissions from coke ovens. For example, OSHA regulations taking effect in 1980 limit employee workday ambient atmospheric exposure to 150 μg (per 8-hr shift) of benzene-soluble fraction of total atmospheric particulate (Ref. 28). This standard must be met by engineering control (emissions control and/or, for example, ventilation). Even 150 μg is not considered a "safe" exposure, according to OSHA. Benzene solubles include established carcinogens, such as polynuclear hydrocarbons (also called polycyclic aromatics) (Ref. 33) and noxious irritants such as phenols, for instance. The emissions from coke ovens include noxious and irritant chemicals, potential carcinogens and criteria pollutants. Trace element emissions and details of organic components are tabulated in Ref. 34.

Relevant analytical techniques have been evaluated by the National Institute of Occupational Safety and Health (NIOSH) (Ref. 35).

Atmospheric emissions are difficult to quantify, because reported measurements vary widely. Reasons include the diversity of coke oven and emission control (Refs. 26 through 32), by variations during duty cycle, and variations due to vagaries of maintenance and quality control. Rather sketchy data in United Nations and USEPA reviews (Refs. 36 and 37) have been combined with Smith's (Ref. 27) and translated to metric tons of Si equivalent in Table A-3. These must be considered as "worst case" estimates, for regulatory standards and enforcement at all levels of government are improving. Air pollution control, particularly in the quenching operation, is more advanced in Europe and USSR than in the U.S., but progress is accelerating now in the U.S. (cf., Ref. 36a). Dry quenching is not yet practical in the U.S., although it is mandatory for new and rebuilt facilities in the USSR and is employed elsewhere in Europe (Refs. 30b and 36a). It has several inherent advantages including reduction in air and water pollution and energy saving.

Water pollution problems are reviewed in the United Nations report (Ref. 36a) as well as in a voluminous U.S. literature. Waste water is often used in wet quenching. Typically this water has been treated by mechanical removal of tars and oils, and steam stripping of phenols and ammonia. Biochemical removal of phenolics, thiocyanates, and cyanides from sour waters is also practiced.

This "cleaned" water, containing residuals, and in excess of quenching recycle requirements is next discharged to evaporation ponds and/or municipal sewers. Dephenolization of waste water can be economically less onerous if phenol, cresols and xylenols can be recovered as marketable byproducts.

Waste water, called "crude ammonia liquor" is also produced in the coke oven off-gas, typically at a rate of about 113 liters/MT coke produced. At the modern Weirton Steel Brown's Island plant, this liquor is stripped in a crude liquor still with a lime teg (Ref. 38).

Additional waste water is generated at the sulfur recovery and light oil plants at the coke batteries.

Biological waste water treatment at Brown's Island requires control of pH, phenols, cyanide, BOD, and temperature. The biological treatment occurs in aerated basins in an activated sludge process said to convert 99% of phenolic wastes to CO_2 (Ref. 38). About 98% of the sludge removed in a clarifier is recycled to the aeration basin; the remainder is discharged to municipal sewers, or trucked to landfill.

Coal

Actual coal-to-coke yields depend on the efficiency of each coke oven facility. As a "worst case" figure, we accept the previously stated ratio of

30 kg metallurgical coking coal to be mined in order to produce 21.4 kg coke (needed to manufacture 1 kg of solar cell Si). This coal may be stripped or deep mined. The potential variety of mining locations and techniques makes it impossible to quantify the environmental impact of the coal mining needed to supply the coke ovens.

Blackwood and Peters (Ref. 39) have measured total respirable particulate emission factors for one unidentified coal surface mine and for one coal storage facility. Translated into kg/MT equivalent Si, their data is presented in Table A-4. We cannot predict the source of coking coal to be used in year 2000, nor do we know how typical these data are of present or future coal stripping. But based on the data of Table A-4, we conclude that coal stripping and coal storage are trivial fugitive particulate emission sources on any national scale, compared with current practice in coke production. Locally, coal stripping and storage can, however, be significant dust sources.

Although mining and reclamation technologies are advancing, there is some evidence that regulatory standards are relaxing at some levels of government.

Briefly, effects of strip mining include:

- Hydrologic Modification (Surface and Subsurface)
- Land Erosion
- Surface Water Siltation
- Decreased pH and Increased SO_4 in Surface Water
- Fugitive Dust Emissions
- Removal of Land from Productivity
- Destruction of Habitat
- Noise Pollution
- Accelerated Road Deterioration
- Indirect Socio-Economic Effects.

Although deep mining appears to be more "benign" than stripping, it can lead to hydrologic modification. Most notable is the well publicized deterioration in water quality due to acid mine drainage from deep drift mines. Currently deep mining is more hazardous than stripping -- both accidents and respiratory ailments contribute to disablements and fatalities. Indirect socio-economic effects also occur. Subsidence and mountainside slumps occur, and contribute to removal of land from productivity.

Both forms of mining create slag heaps ("gob piles"), some of which ignite spontaneously and smoulder for years. Safe and economically attractive means of extinguishing large gob pile fires apparently do not exist. The major noxious combustion product is SO_2. Leachate from coal storage piles as well as gob piles contribute to surface water pollution.

Coal refuse dams are infamous hazards in the aftermath of West Virginia's Buffalo Creek disaster. Aside from such dramatic events, coal fines lagoons generated by coal cleaning plants irretrievably remove some land from future use. Frequently these areas were fertile Appalachian valleys.

Coal cleaning plants are improving. Nevertheless, they are locally significant sources of suspended particulates, fugitive dust, and noise, as well as energy consumers. Coal pile leachate contributes to water pollution.

New source performance standards for coal preparation plants have been promulgated in the Federal Register (Ref. 40). Because these are pollutant concentration (or effect) standards rather than process weight limits, they are not convertible to emission factors without plant-specific information.

Effluent limitations guidelines (ELG) for coal preparation plants (Ref. 41) permit no pollutant discharge. For coal storage, refuse storage, and preparation plant "ancillary areas," the ELG based on BPCTCA lists "concentration" limits on iron, manganese, TSS and pH.

The ELG for acid or "ferruginous" mine drainage (Ref. 42) lists BPCTA "concentration" limits identical to the BPCTA of coal preparation plants. For alkaline drainage, total iron, TSS and pH are also identical. Dissolved iron and total manganese are not listed.

These limitations cannot be translated into kilogram per ton of product.

For definitive discussions of environmental effects and mitigating technologies in the coal mining and preparation sectors, consult Refs. 14 and 43 through 46. A standard annual survey and statistical compilation concerned with coal resources and industries is the Keystone Coal Industry Manual (Ref. 47).

Atmospheric Discharge of "SiO" Dust

SiO dust produced during arc furnace operation is the largest solid waste stream by weight. Like $SiCl_4$, however, it has some potential for by-product utilization, for example, in ceramics and mineral wool insulation production.

The production facility chosen as our basic module, producing 100 MW of Si annually, releases to the atmosphere 1.43 kg/h of SiO dust. The particle size distribution is unknown, and needs investigation. Annual release would be 12.5 MT.

As a solid waste stream, this factory produces hourly about 286 kg of impure SiO comprising:

Substance	Weight (%)
SiO	77.4
Si	14.2
Al	4.3
Ash	4.5
Ti	1.3

Undoubtedly there are trace constituents; Al and Ti may be wholly or partly oxidized; and some of the SiO+Si may be present as SiO_2.

Annual production of this waste stream is 2500 MT. Not only are ceramics and rock wool industries possible customers, but this tonnage may be also attractive to the ferrosilicon industry.

The collected dust has to be handled in closed and exhausted conveyors and transport equipment. Depending on specific end use, the dust could be mixed with water and handled as a slurry.

Silicon monoxide is probably a misnomer. Unquestionably it exists in the gas phase. Normal "SiO" in the condensed phase is known now to be 1:1 Si + SiO_2, unless rapidly dry quenched (Ref. 48).

Rapidly dry quenched "SiO," whatever its composition may be, is a brown, amorphous, pyrophoric solid which burns to SiO_2 in air (Ref. 48). Kolderup (Ref. 49) states flatly that all Si fume and SiO vapor over open submerged arc ferrosilicon furnaces are oxidized to SiO_2 in air.

The implications of this discussion are that: (1) the principal industrial hygiene problem arises from respirable SiO_2; (2) that any air pollution control device which permits a rapid dry quench of Si-SiO fume introduces a fire hazard; (3) any dry collector (such as a fabric filter) should be far enough downstream to absolutely ensure that the fume has been 100% oxidized to SiO_2 prior to collection; and (4) a wet scrubber would eliminate any fire hazard due to pyrophoric dust if (3) is not a practicable solution.

It is possible that occasional baghouse and flue fires may occur (and may have occurred) due to SiO accumulations. Kolderup and other writers do not comment on this point. X-ray diffraction laboratories can distinguish positively and rapidly between amorphous SiO dust and polycrystalline SiO + Si dust. Such laboratory analyses are not suitable for continuous flue gas monitoring, however. Development of some sort of ignition or flammability test on samples continuously extracted from ventilation hood ducts seems to offer some promise if control device fires become a problem.

The Norwegian ferrosilicon alloy industry is a major source of experience in silicon alloy production and fume control. Ferrosilicon production there is one of the most important sources among all industrial fume releases (Ref. 49).

In the U.S., however, in a ranking of particulate pollutant releases by various measures of objectionability (Ref. 50), Si and ferrosilicon production received no specific ranking at all among major sources based on:

Community Complaints
Increased Ambient Urban Background Toxicity
Soiling
Materials Deterioration
Relation to Federal and State Air Quality Goals
Overall Objectionability.

Nevertheless, Si production in submerged electric arc furnaces presents important and difficult air pollution control problems.

Chief reasons are (Refs. 49 through 51):

- Large Gas Volumes
- Small Particle Size (0.01 to 4.0 μm)
- Proportional Relationship with Power Consumption
- High Electrical Resistivity ($> 10^{10}$ ohm-cm)
- High Emission Rates (290 kg/MT)
- Discontinuous Emissions Due, for Example, to Charging Cycles.

In this industry, power consumption (rather than product tonnage) is the conventional measure of capacity.

In 1971 only two U.S. plants were devoted exclusively to Si production. Located in Oregon and Alabama, both were small – less than 25,000 kW (Ref. 51). Although some larger U.S. plants, located in Washington and Ohio, exceed 75,000 kW, they produce other alloys in addition and their Si capacity is unknown. The module used in this report is 17,000 kW. This is typical of Si-only facilities in the U.S.

Figure 8 is a stylized view of an open submerged arc furnace. Details vary from the air pollution control point of view. The most important likely variations are the semi-closed furnace and the sealed furnace (cf., Refs. 50 and 51). Many aspects of air pollution control in Si production are discussed in elaborate detail in the two references cited above, and will not be repeated here.

Table 5 presents ground-level particulate concentrations which may occur at the stated distances from a silicon furnace. Table 6 shows for comparison, the National Primary and Secondary Standards for particulates.

The method of arriving at the data of Table 5 clearly is crude (cf., footnote). Further, the figures given for 0 km relate to industrial hygiene, rather than environmental quality.

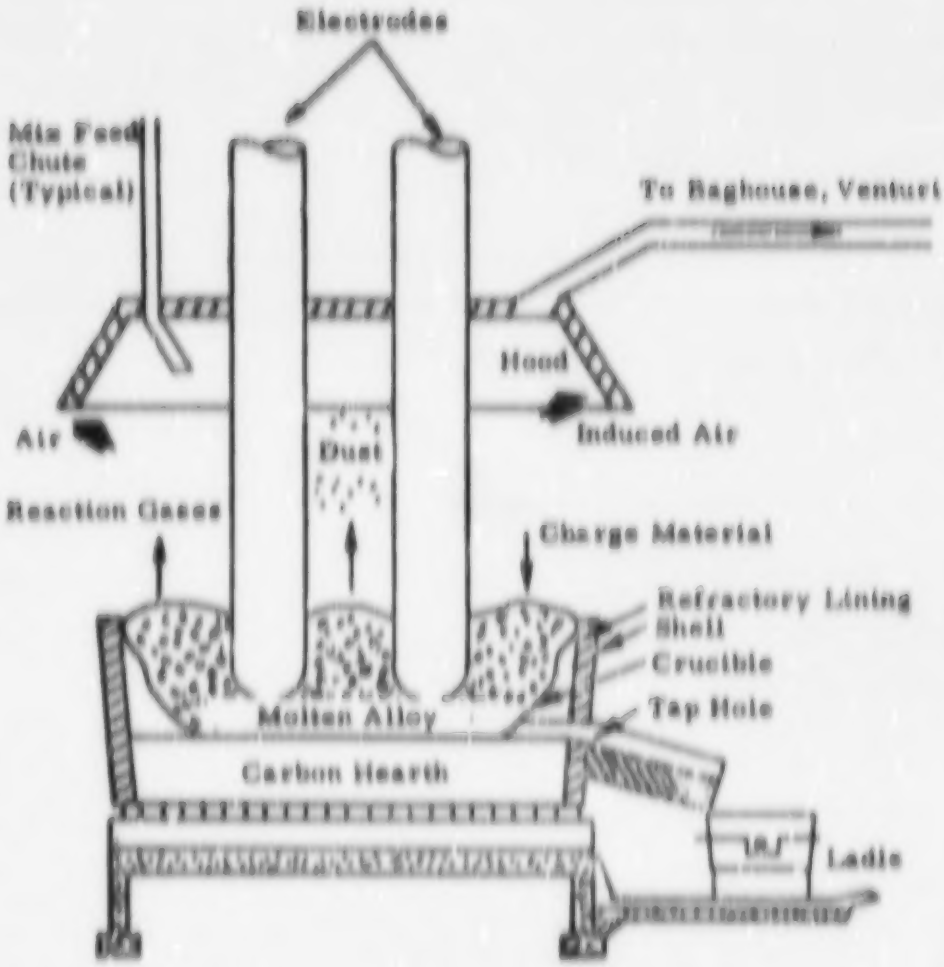


Figure 8. Submerged-arc furnace for silicon production (Ref. 51 modified)

TABLE 5. ESTIMATED GROUND LEVEL PARTICULATE CONCENTRATIONS CAUSED BY 17,000 kW OPEN SUBMERGED ARC SILICON FURNACE WITH BAGHOUSE COLLECTION.

Emission Rate (kg/h)	Averaging Times	Estimated Ground Level Particulate Concentration at Specified Distance from Source ($\mu g/m^3$)[a]			
		0 km	0.5 km	5.0 km	20 km
2.51[**]	24 hr	875	117	12	1
	1 yr	117	15	1	--

[a]Obtained by down-scaling from data for a 7.92 kg/h source given in Ref. 51.

[**]SiO plus flyash from furnace hood baghouse.

TABLE 6. NATIONAL PRIMARY AND SECONDARY AMBIENT AIR QUALITY STANDARDS FOR PARTICULATE MATTER (REF. 53)

Time Period	Concentration, $\mu g/m^3$	
	Primary Standard	Secondary Standard
24 hr[*]	260	150
1 yr[**]	75	60[†]

[*]Maximum 24-hour concentration not to be exceeded more than once a year.

[**]Annual geometric mean.

[†]To be used as a guide in assessing implementation plans to achieve the 24-hour standard.

Nevertheless, we see at 0.5 km that the additional atmospheric particulate burden contributed by a single silicon submerged arc furnace is comparable in magnitude to the secondary 24-hr standard and nearly half of the primary 24-hr standard.

Ferrosilicon and Si facilities commonly will be located in urban industrial areas which already have many particulate sources. Unquestionably,

additional Si submerged arc furnace capacity in the U.S. will adversely impact achievement of air quality goals. The fraction of such furnaces actually ascribable to solar cell Si is irrelevant.

New Source Performance Standards for Ferroalloy Production Facilities (including elemental Si) were promulgated on May 4, 1976 (Ref. 53). Paraphrased, those standards are:

NEW SOURCE PERFORMANCE STANDARDS
SILICON PRODUCTION IN ELECTRIC SUBMERGED ARC FURNACES
(PARAPHRASED FROM REF. 53)

STANDARDS FOR PARTICULATE MATTER

Mass Loading – gases shall not exit from a control device and contain particulate matter in excess of 0.45 kg/MW-hr while silicon metal is being produced.

Opacity – gases shall not exit from a control device and exhibit 15% opacity or greater. Nor shall there be discharged into the atmosphere from any dust-handling equipment any gases which exhibit 10% opacity or greater.

Visible Emissions – gases shall not exit from an electric submerged arc furnace and escape the capture system and be visible without the aid of instruments during periods when flow rates are being established. Nor shall gases escape the capture system at the tapping station and be visible without the aid of instruments for more than 40% of each tapping period. (There are no limitations on visible emissions under this subparagraph when a blowing tap occurs.) The requirements under this subparagraph apply only during periods when flow rates are being established.

These mass loading restrictions would permit short term emissions at the rate of 7.65 kg/hr from the 17,000 kW furnace in our model plant. The average emission rate we have stipulated is 2.31 kg/hr (SiO and fly ash combined). This leaves little allowance for transients, failure of control equipment to meet specifications, operator error and maintenance lapses, etc.

We conclude that this 17,000 kW reduction plant would comply with current NSPS for SiO plus fly ash, and by itself would not cause airborne particulate loads to exceed national primary and secondary ambient air quality standards. At the same time, the safety margin for NSPS compliance is not large. Further, it would be difficult to continue in compliance with National Primary and Secondary Air Quality Standards in regions or communities in which new submerged arc furnaces typically would be installed.

If a venturi scrubber or other wet collector is used in addition to or in lieu of fabric filters, there are Effluent Limitations Guidelines (ELGs) which

are applicable (Ref. 54). However, these limitations are aimed primarily at the chromium and manganese released in ferrochrome and ferro manganese production. Those portions of the ELGs relevant to Si open electric furnaces are:

Effluent characteristic	Maximum for any 1 day	Average of daily values for 30 consecutive days shall not exceed —
		kg/MWh
		BPCTCA
TSS	0.319	0.160
pH	Within the range 6.0 to 9.0	
		BATEA
TSS	0.024	0.012
pH	Within the range 6.0 to 9.0	

The "Best Available Technology Economically Achievable" (BATEA) limits apply to New Sources. The TSS limits translate to 194 (BPCTCA) and 14.6 (BATEA) kg/MT solar cell silicon.

Si Dust

Depending on end use, Si fines from cutting and shaping operations in later production steps may be combined with the SiO-Si fines waste streams described above.

Recycle of Si and SiO

The combined Si-SiO waste stream represents 182 kg/h elemental silicon or 389 kg/h pure SiO_2. This is about 25% of the quartz feedstock. With due attention to progressive accumulation of undesirable contaminants, serious attention should be given to recycling this material to the submerged arc furnaces.

SiO and Si fine particulates are low-density, excellent insulating materials. Fine silica particles are presently being sold for high quality thermal insulation. This material could also be used as lightweight filler in concrete or bricks.

Carbon Monoxide

All CO is expected to be combusted in a waste heat boiler. Flares are also usable. The relevant NSPS is given in Ref. 52 and no compliance problems are anticipated.

Oxides of Nitrogen

No provisions of the NSPS relate to NO_x. The model plant will emit 10.84 kg/h from its waste heat boiler. Although this is low, it could be reduced further by combustion modifications. Flue gas scrubbing for NO_x is not yet common, and does not seem economically justifiable for this source.

Sulfur Dioxide

The sulfur content of the coke used in the arc furnace would exit the process as SO_2 from the waste heat boiler. The concentration is very low, dependent on coke sulfur content, and may be low enough to meet environmental standards without further treatment. There are no standards for SO_2 or SO_x in the NSPS for electric submerged arc furnaces. The SO_2 concentration in the combustion gases from the waste heat boiler will be 0.91 g/m^3, assuming the nominal coke composition listed on the flow sheet. However, actual mass of SO_2 discharged hourly is less than 10 kg/h.

Methods of reducing SO_x include coal cleaning prior to coking, using the lowest-sulfur metallurgical coals available, and flue gas desulfurization.

Fluorine Compounds

SiF_4 gas is produced by the etching reaction of HF-HNO_3 on the wafer. At present, the best method of removing the gas is reaction with $Ca(OH)_2$ in a wet scrubber, producing CaF_2, which is relatively insoluble (~20 ppm). The CaF_2 may be placed in a land fill.

Alternatively, a recycle market may develop, since the CaF_2 may be rather pure compared with domestic fluorite deposits. Higher grade fluorspar (fluorite) mined in the Rosiclare and Cave-in-Rock districts, Illinois and Kentucky, and Northgate district, Colorado, for example, are now used in the metallurgical and glass industries. Metallurgical grade fluorspar must contain at least 85% CaF_2, certainly obtainable from this process (Ref. 55).

Domestic resources of fluorine are estimated at 5.4×10^6 MT. Based on the present ratio of domestic production to demand, the presently known U.S. resources of fluorine in the form of fluorspar will be depleted in 25 to 30 years (Ref. 56). This suggests that by year 2000 there will probably be greatly increased emphasis on byproduct fluorine recovery in all segments of industry.

Environmental Effects of In Situ Damage

Silicon solar cells are non-toxic and stable. If massive damage to solar panels occurs, the potential environmental effects would be limited to disposal of debris.

ENERGY AND ENVIRONMENTAL SUMMARY

Table 7 summarizes emission factors (kilograms of pollutant per metric ton of solar cell Si) and total mass of pollutant emitted annually. The latter value is based on a solar cell production rate of 4500 MW of solar cell Si manufactured annually. For comparison, Table 8 presents the mass of primary pollutants from 9000 MW_e coal fired steam electric generation. In Table 1 we saw that 4500 MW of Si cells would, at steady state, maintain 9000 MW_e electric generating capacity.

In Table 9 the data of Tables 7 and 8 are organized differently in order to illuminate the air pollution impact of Si solar power generation. We see that:

- Particulates generated directly in Si and Si-cell manufacture (910 MT/yr) represent only 68% of the total resource and manufacturing-generated particulates (1410 MT/yr).
- The very large power demands of Si and cell production add an additional, and overwhelmingly more important contribution (approximately 12,100 MT/yr).
- When mining, manufacturing, and power generating are considered together, we see that Si photovoltaic power seems to be "57% as dirty" as coal-fired power.
- With respect to SO_x and NO_x, Si photovoltaic power is "57% and 53% as dirty," respectively, as coal-fired power.

The reader should realize that our numbers for coal-fired emissions do not include any secondaries (coal mining, steel and cement manufacturing, etc.), while those for Si do. This is not basically why the comparison seems unflattering to Si, however.

Basically, the problem is that Si production is hugely energy intensive. Any improvement in technology which significantly improves the energy efficiency of Si production is likely to make major reductions in net atmospheric pollution. This becomes obvious when we make the comparison as in Table 10.

Other pollutant releases are not directly comparable. The very large quantity of oils and lubricants would not be released to natural waters; consequently no comparison can be made fairly with the 304 MT/yr oil and grease discharges from coal-fired plants.

TABLE 7. PRIMARY AND SECONDARY POLLUTANTS RESULTING FROM 4500 MW/YR SILICON SOLAR CELL PRODUCTION

	kg/MT Solar Si	MT/yr (4500 MW/yr)
QUARTZITE MINING		
Atmospheric Particulate[a]	11.53	129.0
Wastewater[b]	ND	ND
COAL STRIPPING		
Atmospheric Particulate[c]	0.19	6.3
Wastewater[c]	??	??
COAL STORAGE		
Atmospheric Particulate[c]	0.20	6.3
Wastewater	??	??
COAL PREPARATION		
Atmospheric Emissions	?	?
Wastewater	?	?
COKING[d]		
Atmospheric Emissions		
Suspended Particulate	87.3	310
SO_2	11.6	131
CO	1.8	21
Total HC	??	??
Aromatic HC	0.8	9.4
CH_4	0.5	7
H_2S	0.8	10
Cyanides (as HCN)	1.1	13
Phenols	0.5	7
Pyridine Bases	0.004	0.04
Tars	??	??
NO_x	??	??
Wastewater	?	?
SILICON AND SILICON CELL MANUFACTURE[e]		
Atmospheric Particulate	86	960
Gaseous Emissions		
CO_2	710000	7950000
HCl_3 (as HCl)	180	4000
NF_3	180	4000
Liquid Wastes		
Oils and Lubricants	8000	90000
Aqueous H_2SiO_3	180	4000
Solid Wastes		
Si	1403	28000
SiC	7302	87000
Flyash	763	1000
Ti (Unknown Oxidation State)	170	2000
Al (Unknown Oxidation State)	3100	6000
Sb	8000	89000
CO_2	8000	87000
Dopd	7700	86000
Adhesives	180	2000
$AsCl_3$	1400	16000
CaF_2	??	??
Phosphorus Residues	Trace	Trace

[a] See Table A-3 for elemental composition. Datum is for quartzite quarrying.

[b] Based on EPCTCA guideline for sand and gravel mining and processing.

[c] See Table A-6.

[d] Known pollutant, but no numerical data available.

[e] Available data, limitations, or standards are expressed in terms of effluent concentration and cannot be converted to mass emissions or discharges (see text).

[f] Byproduct slot ovens with "control" and not quench. Much domestic coke capacity is without control.

[g] Excludes "wastes" destined for byproduct utilization. Some pollutants have been recombined into different categories than those in which they appeared in Table 3.

TABLE 5. PRIMARY POLLUTANTS FROM 9000 MW_e* POWER FROM COAL FIRED STEAM PLANTS

Pollutants	Emissions**, MT/yr
Air	
SO_x	2.86×10^5
Particulates	0.24×10^5
NO_x	1.67×10^5
Cd	0.43
Water	
TSS	608
Oil/Grease	304
As	143
Cd	10.0
Cr	7.88
Cu	0.36
Fe	0.36
P	197
Pb	106
Se	42.6
Zn	39.4

*1% of projected electricity generation capacity for the year 2000.

**Emission factors for coal fired plants assume the application of the control technology in the relevant NSPS and Effluent Limitations Guidelines (Ref. 57) and Development Document (Ref. 58). Trace metal emission factors were derived from recent literature (Refs. 59, 60).

TABLE 9. COMPARISON OF THREE CRITERIA POLLUTANTS AS EMITTED IN SILICON CELL AND FEEDSTOCK PRODUCTION, AS EMITTED IN ELECTRIC POWER GENERATION TO SUPPLY SOLAR CELL PRODUCTION, AND AS EMITTED BY 9000 MW_e COAL-FIRED POWER GENERATION.

Pollutant and Source	MT/yr: Solar Cell Silicon Mfg.	MT/yr: 9000 MW Coal-Fired Power*
Atmospheric Particulate		
SiO_2 Mining and Processing	129.0	
Coal Stripping	8.1	
Coal Storage	2.5	
Coal Preparation	**	
Coke Production	310.0	
Silicon and Si-Cell Mfg.	960.0	
Subtotal	1,409.5	
Power to Produce Si and Si Cells†	12,100.	53,800
Total	13,500	
Sulfur Oxides		
Coke Production	131.0	
Silicon and Si-Cell Mfg.	4,000.	
Subtotal	4,131.	
Power to Produce Above†	145,400.	
Total	149,500.	886,000
Nitrogen Oxides		
Silicon and Si-Cell Mfg.	4,000.	
Power to Produce Above†	84,900.	
Total	88,900.	167,000

*Includes primary (direct) pollutants only, and none of the secondaries.

**Available data, limitations, or standards are expressed in terms of effluent concentration and cannot be converted to mass emissions or discharges.

†See Table 8. Assumes coal-fired power.

TABLE 10. SILICON RELATED EMISSIONS AS % OF EQUIVALENT COAL-FIRED EMISSIONS.

	Silicon Related Emissions as % of Equivalent Coal-Fired Emissions		
	Particulates	SO_x	NO_x
Including Si Power Demand	56.7	50.8	53.2
Not Including Si Power Demand	4.9	1.4	2.4

Quantities of cooling water are required for the model 4500 MW solar cell production level economy. In all, 79.5 x 10^6 kg/h of cooling water is needed, discharging waste heat equivalent to a single 3500 MW power plant. This is less than, but not trivial compared to 9000 MW_e coal-fired power plant needs.

The total power delivered to this plant, from outside generating stations, is 4574 MW. These outside generating stations reject waste heat, also. To a crude approximation, the total waste heat rejection, inside and outside the plant, is about that of an 8074 MW power plant. This should be compared to the 9000 MW generating capacity the silicon is meant to replace.

Again, we see that any successful efforts toward improving energy efficiency of Si production are likely to have substantial environmental benefits.

In a comparison report (Ref. 61) we examine the materials requirements consequent to actually using Si solar cells. For a 1000 MW_{pk} silicon photovoltaic plant with concentration and one-axis tracking the following major structural materials would be needed:

835,000 MT steel (for structures)
260,000 MT cement (for foundations)
164,000 m^3 water (for concrete)
2,400 MT Li (for batteries)

In any thorough-going assessment of residuals, extraction and manufacture of such materials must be included, both for solar and for its alternatives.

IMPACT ON NATURAL RESOURCES

Production of arrays which will put out 4500 MW (peak) using 0.15 mm thick, 14% efficient, Si solar cells with overall production yield of 34.8% requires 32.14 x 10^6 kg of pure polycrystalline Si. This is about 25 times the estimated total semiconductor Si production in 1974 and 38% of the 1968 United States production of 99% pure Si (metallurgical grade). The U.S. reserves of SiO_2 which may be used to produce Si are so great that they have not been completely cataloged.

POLLUTION CONTROL TECHNOLOGY READINESS AND PROJECTIONS

A reduction in Si requirements may result if technological improvements can be realized: (1) increased utilization of Si, that is, more area from a given mass of Si, and (2) increased efficiency-more output/area. In the ERDA-JPL Low Cost Silicon Solar Array Project (7), Task II, the problem of obtaining increased utilization of Si is approached several ways. Of these the most promising are: (1) upgrading the single-crystal ingot cutting used in this study, which also yields more area at higher efficiency, (2) edge-film-growth (EFG) of ribbons, and (3) chemical vapor deposition of polycrystalline Si which produces the greatest area but very low efficiencies.

Of these, only the latter will make a significant reduction in Si requirements. But that reduction will occur only if cells of greater than 5% efficiency can be produced - assuming 15 μm thickness and 50% utilization of polycrystalline Si.

Edge-film growth of ribbons offers some labor economies in producing area but the yields are not significantly better than ingot slicing and problems in producing cell quality ribbon need to be overcome. Sliced single-crystal ingots offer the best near term potential for both increased material utilization and higher efficiency.

During wafer slicing the major environmental problems are: (1) safeguarding employees from breathing aerosol oils containing SiC abrasive, and (2) handling and disposal of the sludge which contains oils, clay, alumina, adhesive, abrasive, Si and steel. Currently the employees are protected by placing an exhaust fan over the saw to collect the vapors and pass them through an expanded metal screen which traps them. This method appears to be adequate for current levels of production. However, more effective methods such as fabric filtration may be required for large scale production. Disposal of cutting sludge should involve extraction of oils for recycling before disposal into land fill.

The $HF-HNO_3$ etching of the Si prior to remelting produces SiF_4 gas. The handling and disposal involves collection of the gas and passing it through $Ca(OH)_2$ to produce CaF_2 which is relatively insoluble in water. Current methods of collection, neutralization, sampling and disposal appear to be technically adequate. It remains to scale them up to handle the increased volumes which will result from large scale production.

Wafer diffusion involves PH_3 gas in small quantities which are significant from an occupational health standpoint. No environmental problem seems to exist outside plant perimeters. The chemistry of the diffusion reaction and resulting products is not completely understood, but appears to be adequately controlled for current production levels. Other products containing phosphorus collect on the furnace tube near the exit. With increased production these probably would be economically recycled.

ENVIRONMENTAL CONSEQUENCES AND CORRECTIVE ACTIONS – SILICON

High energy consumption for Si rod deposition	R&D on process improvement
HF removal of oxide for recycle of ingot to remelt and SiF_4 generated present potential personnel hazard	Recommend safe handling methods and safety devices. Scrub SiF_4 with $Ca(OH)_2$
Phosphine gas during wafer diffusion and waste disposal	Recommend handling methods and safety devices to protect personnel
Si and abrasive dust in oil aerosols	Limit personnel exposure by venting and filtration
"$SiCl_4$" byproduct stream	Develop effective technique for converting Si fluorides to $SiHCl_3$ as part of an in-plant recycle stream
SiO in dusty off-gas	Determine if SiO is true composition, and if it constitutes fire hazard in dry collectors. If affirmative, develop on-line SiO monitor, and provide appropriate collection system modifications.

SECTION 5

CADMIUM SULFIDE PROCESS

GENERAL PROCESS DESCRIPTION

Raw Materials

The main source of cadmium for all cadmium alloy products is the smelting and refining of zinc ores (Refs. 62 and 63). The cadmium by-product concentrates are in the form of fumes from zinc calcine sintering plants (pyrohydrometallurgical zinc refining) or precipitates from zinc electrolyte in electrolytic zinc refining. Details of the principal techniques used in mining and refining zinc ores and separating the cadmium-rich streams are given elsewhere (Refs. 61 through 67). The environmental impact of this processing (Refs. 64, 65, 67 and 68) will not be considered, however, because these emissions would exist whether or not cadmium was used as a byproduct for solar cells.

The other important feedstock in the production of CdS is raw sulfur. Readily available emission factors from the manufacture of sulfur by the Claus process indicate that sulfur dioxide is the major environmental problem. SO_2 emissions from uncontrolled Claus plants are 62 to 167 kg/MT of sulfur produced or 4 kg/MT from a controlled source (Ref. 69).

Secondary raw material requirements include process water, fuel oil and make up quantities of sulfuric acid and argon. Hydrocarbon vapors emitted during the storage and transfer of fuel oil are 0.21 kg/1000 liters of fuel oil (Ref. 69). The Environmental Protection Agency performance standard for SO_2 from sulfuric acid plants is 2 kg/MT of 100% sulfuric acid, while the standard for acid mist emissions is 0.075 kg/MT of acid (Ref. 70).

Substantial quantities of structural and protective materials are also required to support the CdS photovoltaic material. These will include copper, glass, zinc, lead and stannous oxide. Emission factors associated with the mining, smelting, refining and finished production of these materials can be estimated from (Refs. 58, 64, 65, 68 and 69). This has been done for each of these materials and the results are given in Table 11. In all cases, the emission factors were determined by assuming that the most advanced[b] control technology is applied since the manufacturing will be done in the last decade of this century.

[b] Depending on the information available, emissions were estimated with the application of: NSPS, BATEA, BPCTCA, other controls, no controls; in decreasing order of priority.

TABLE 11. EMISSION FACTORS (kg/MT OF SUBJECT MATERIAL) FOR RAW MATERIALS REQUIRED IN THE PRODUCTION OF GaS SOLAR CELLS[a]

	Air Emissions			Water Effluents								
Materials	SO_2	Dust[b]	HC[c]	TSS	Oil	As	Cd	Cu	P	Pb	Se	Zn
Copper	250	3	–	0.005	0.002	0.562	–	0.00005	–	–	0.001	0.001
Lead	9	40	–	0.02[1]	–	–	0.0004	–	–	0.0004	–	0.004
Zinc	104	7	–	0.14	–	0.00054	0.0027	–	–	–	0.027	0.027
Stannous Oxide			Unknown					No Discharge				
Glass	–	1	–	0.7	1.4	–	–	–	0.05	–	–	–
Fuel Oil (Trans. and Storage)	–	–	0.0003					Unknown				
Sulfur	2	–	–					No Discharge				
Sulfuric Acid	2	0.075	–					No Discharge				

[a]Emissions include those from mining, refining, producing and transporting materials as available information permits. When information was missing or in the wrong form (i.e., some NSPS effluent limitations are in terms of maximum effluent concentration, mg/l, rather than waste factors, kg/MT of product), zero discharge was assumed. Also factors were derived from varying degrees of control. The control level utilized was selected in the order of decreasing priority from: NSPS, BATEA, BPCTCA, No Control. Emissions associated with the densified, cadmium-rich fumes (from the mining, milling and smelting of sinclare ignored.

[b]Particulates, acid mists, fly ash, etc.

[c]HC = hydrocarbons.

Process Description

Cadmium extracted from zinc concentrates is a starting material for the process assumed for this study. The recovery of cadmium and other byproducts in the zinc refining industry is receiving increased attention because of pollution considerations. A recent comprehensive EPA report (Ref. 71) and an industry survey by the Bureau of Mines (Ref. 72) describe the principal processes in refining Cd and quantify pollutants and cadmium availability. The process flow diagram and material and energy balance for producing pure Cd, shown in Figure 9, is based on a hypothetical "Byproduct Cadmium Subsystem" (Refs. 66, 71 and 72).

In Figure 9 cadmium processing begins with receipt of densified cadmium fume from the roasting and sintering of zinc concentrates, which is considered a necessary part of zinc processing. The chief constituents are the oxides of zinc, cadmium, lead and copper; relative quantities of these constituents are given for illustrative purposes. Expected contaminants are listed, and, where possible, the chemical state, combined anions and relative concentrations of the emissions are identified. The Cd fume is collected and wet-milled and leached with sulfuric acid to extract cadmium and other acid soluble components.

Lead sulfate, silver, gold and trace metals remain as solids and are filtered out. The sulfate liquor is then neutralized with zinc oxide which precipitates oxides of antimony and arsenic and hydroxides of cobalt, nickel and thallium. Sodium chlorate oxidizes ferrous ions to ferric which are precipitated as $ZnO\text{-}Fe_2O_3$.

The antimony and arsenic oxides in the above precipitate are a potential problem; therefore the filter cake should be either processed further for byproducts or collected in an environmentally safe landfill.

The filtrate is next treated with a limited amount of zinc dust to precipitate copper, but not cadmium. After centrifuging to remove the copper, more zinc dust is added which precipitates the cadmium sponge, which is then washed to remove zinc sulfate, briquetted and purified by distillation. The oil-fired retort will emit stack gases from combustion with air; and entrained cadmium fines ($\leq 8\ \mu$) which are rapidly oxidized (Ref. 67). The waste washwater containing very low concentrations of zinc sulfate and cadmium can be sent to an evaporation pond. Sites for and amounts of cadmium losses exhibited in Figure 9b were determined from pages 272, 273, and 382 of Ref. 67.

Since sulfur and sulfuric acid are already produced in large quantity and are available in high purity, solar cell production is not expected to significantly affect those industries. In addition the zinc smelting process produces SO_2 which can be used to make sulfuric acid which is consumed in leaching of the cadmium fume.

The pure cadmium sulfide is produced by directly reacting cadmium vapor, in an argon gas carrier, with sulfur vapor in a reaction tube. CdS is condensed in the cool end of the tube and excess sulfur is condensed at a

Figure 4a. CAS process flow diagram

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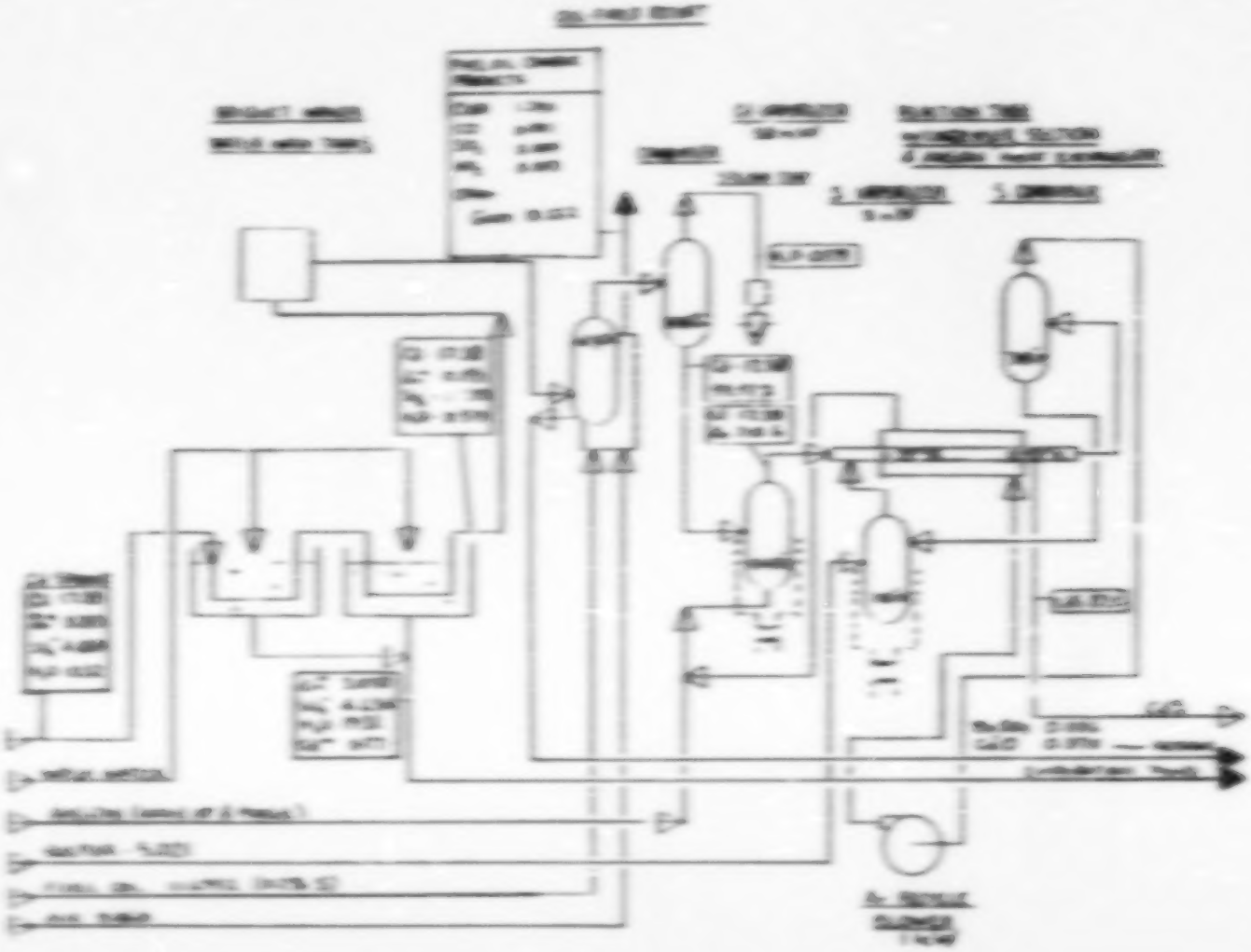


Figure 9b. CdS process flow diagram.

lower temperature from the argon stream. In the hypothetical process shown, argon is recirculated and used to cool the reaction tube since the CdS formation is exothermic.

CdS/Cu_2S Solar Cell Production

Two processes have been proposed for large scale production of CdS/Cu_2S solar cells. The back-surface cell process forms the cell by spraying reagents on the back of glass sheet emerging from the "float glass" manufacturing process. The second process forms the cell on the front surface of thin metal foil with vacuum deposition of the compounds to form the heterojunction and collection grids. Cross sections of the two cell types follow in Figures 10 and 11, respectively. Neither of these has progressed beyond laboratory proof-of-concept experiments. However, there appear to be no significant technical problems preventing their implementation.

The pollution problems arising from these processes have not been examined fully because of uncertainty of process details. For this study we have attempted to identify the hazardous chemicals and suggest further efforts to assess environmental aspects as process details are developed.

Efficiencies as high as 9 to 10% may be achieved if several chemical and production problems can be solved. Laboratory samples have been produced on a batch basis with maximum efficiencies of 5%.

Lifetimes for CdS solar cells are limited by several factors not currently understood (Ref. 73). For this study we have projected a 5-year lifetime at 5% efficiency for both cell types.

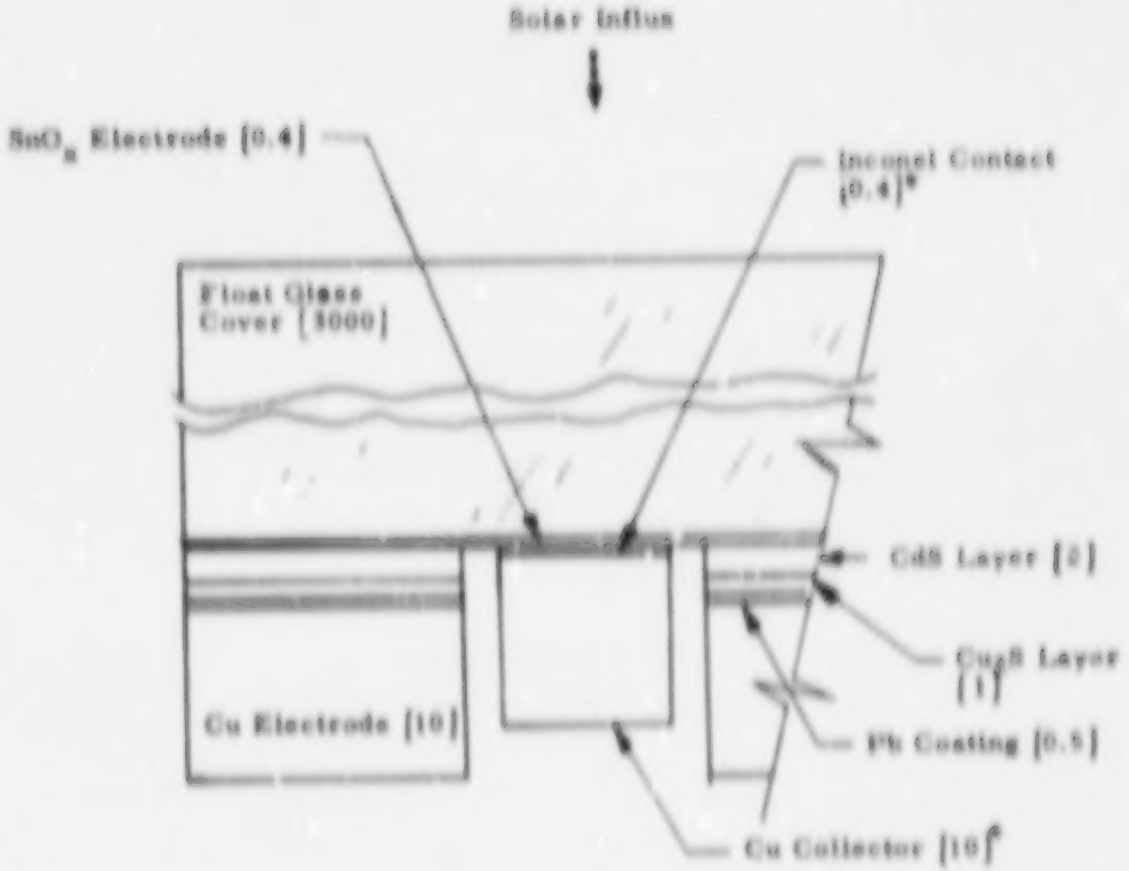
Back Surface Cell-Spray Processing (Refs. 74 and 75)--

The back surface cell is being developed by D. H. Baldwin Company, El Paso, Texas. It uses common window glass as the cover on which the active layers of CdS and Cu_2S are sprayed while the float glass cools, see Figures 10 and 12.

There are three spray stations which sequentially form a conductive layer of tin oxide, the CdS layer, and the Cu_2S layer. The exact compounds used in each spray process are proprietary to the Baldwin Company. From their report, we know that a salt of tin plus other chemicals are used to form the SnO_2 layer and that $CdCl_2$ and thiourea plus other chemicals are used to form the desired CdS layer. Also, a combination of copper acetate and N,N, dimethyl thiourea plus other chemicals are used to form the Cu_2S barrier. No other data are available on this process, except that Refs. 74 and 75 state it will be necessary to scale up the process before dealing with the pollution problems arising from the spray process.

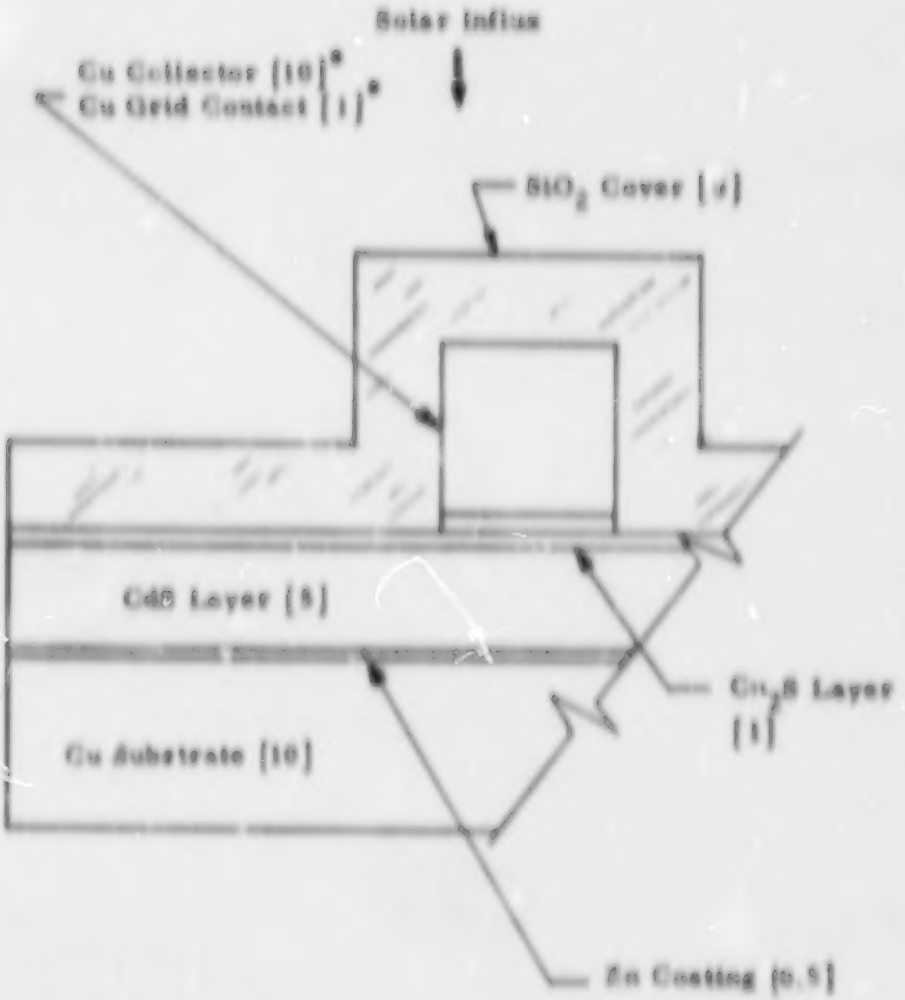
Front Surface Cell-Vacuum Processing (Ref. 76)--

The front surface cell, developed by Westinghouse, is manufactured in sequential stages inside a large vacuum chamber. It consists of a 0.5 micron zinc coating on 10 micron copper foil substrate, a 5 micron thick CdS layer,



[ ] Thickness (10^{-6} m)
* Cover 15% of Cell Area

Figure 13. Cross section – back surface CdS cell.



[ ] Thickness (10^{-6} m)

* Cover 15% of Cell Area

Figure 11. Cross section of front surface CdS cell.

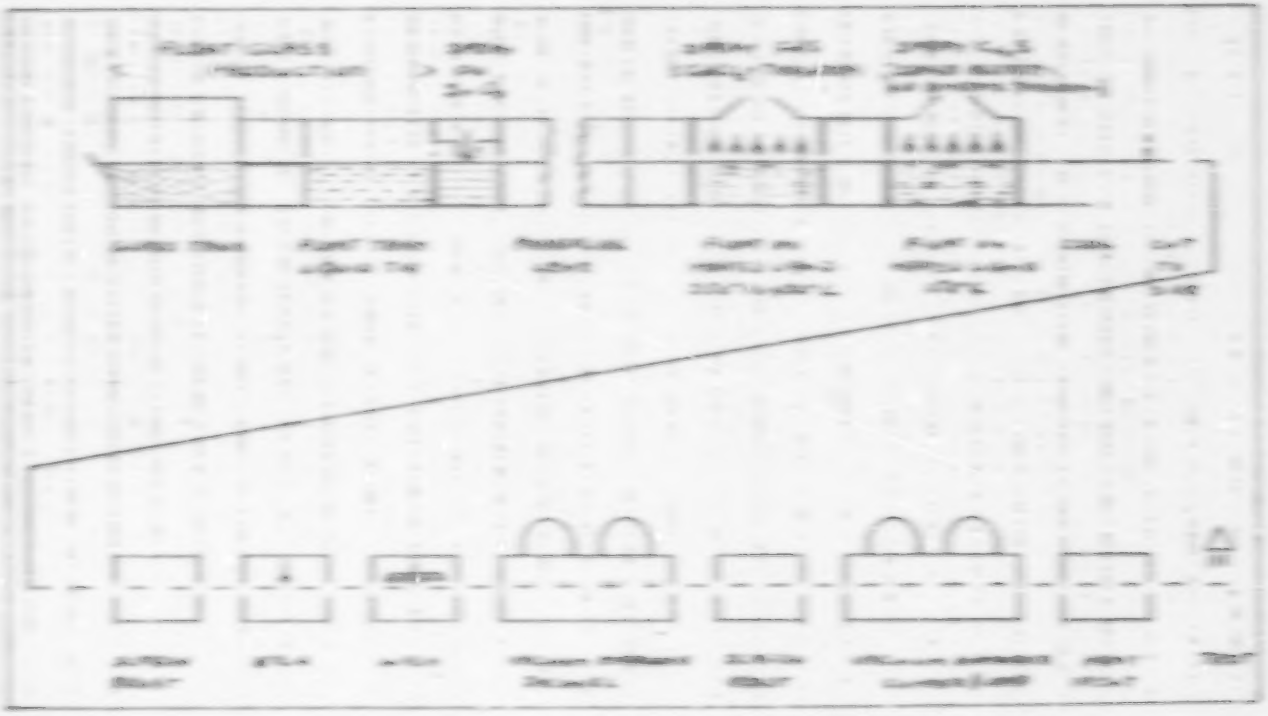


Figure 12. CdS solar cell production — back surface cell-spray process.

a 0.5 micron Cu_2S barrier layer, a 1 micron copper grid contact and 10 micron copper collector bus, and a protective cover of 5 microns of sputtered SiO_2 as shown in Figures 11 and 13. Except for vapor degreasing of the substrate and grid material, all processes are in vacuum. Hydrocarbon emissions from the degreasing process will have to be collected in hoods and treated. The other effluents are contained within the vacuum chamber which require periodic cleaning and removal of the wastes. However, most of these effluents should be of sufficient purity to be recycled.

Because this cell method is only in a proposal stage, little is known about the process details or environmental consequences which would result from large-scale production.

MATERIAL CONSUMPTION AND PRODUCTION ESTIMATES

Assuming that U.S. electric power generating capacity for the year 2000 will be 900,000 MW (average) the quantities of material required for the two cell processes are based on the following assumptions:

1. 1% (average) of generating capacity is equivalent to 65,000 MW (peak), using 5 to 1 peak to average output as shown earlier.

2. Five-year service life means that 9000 MW of cells must be produced each year. This is twice the amount required for Si for which a 10-year service life was assumed.

3. 5% cell electrical conversion efficiency (compared with 10% for Si). This requires that 1.8×10^8 m^2 of cells be produced each year.

The quantities of material required for production of 9000 MW of front surface cells and 9000 MW of back surface cells are shown in Tables 12 and 13, respectively. Quantities for front surface cells are based on processing yields taken from Ref. 75. No process yields were available for back surface cells; therefore conservative yield factors were estimated and shown in Table 13. Quantities in both tables are based on estimated cell area coverage and thickness.

Note that the quantities are based on end product materials in the cells. The process chemical quantities are not shown because they were unavailable due to developmental and proprietary status.

POWER REQUIREMENTS

The energy requirements for the production of some basic materials used in CdS cell production are listed in Table 14. The data are limited which reflects the level of development and the proprietary interests of the developers.

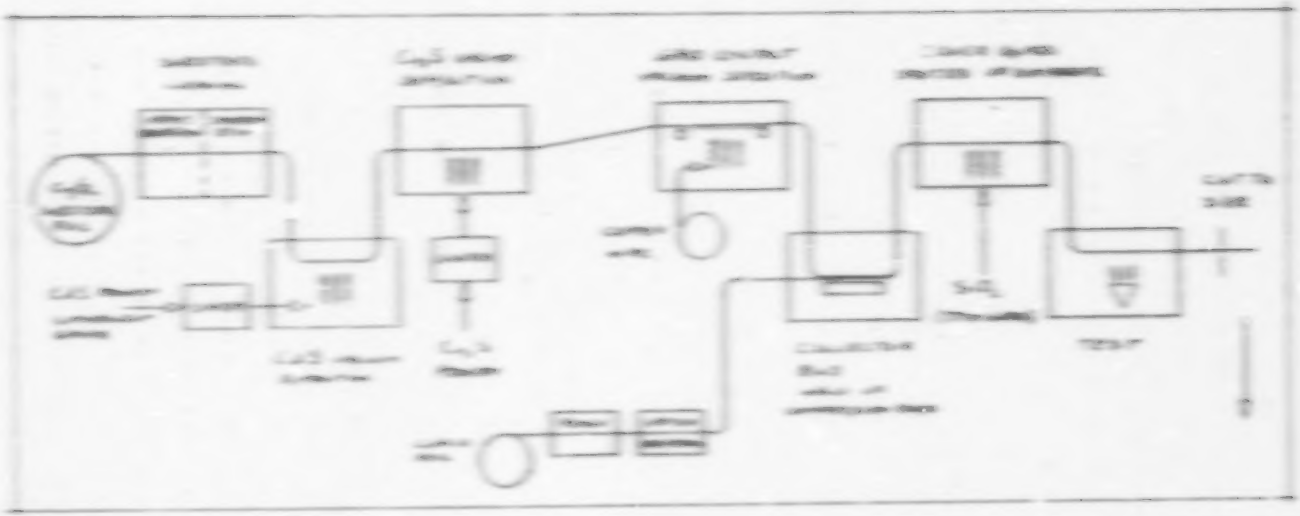


Figure 11. CdS solar cell production – front surface cell-vacuum process.

TABLE 12. QUANTITIES OF FRONT SURFACE CELL MATERIALS FOR 9000 MW/YEAR (PEAK).

Material End Product	Use	Thickness (microns)	Overall Process Yield (%)	Amount Required (Metric tons)
Copper	Substrate	10	75	88,000
Copper	Grid Contact	1	84	860
Copper	Collector Bus	10	75	3,360
			Total Copper	85,000
Zinc	Substrate Coating	0.5	75	890
CdS	Semiconductor	5	80	7,300
Cu_2S	Barrier	1	80	1,300
SiO_2	Cover	5	80	5,000

TABLE 13. QUANTITIES OF BACK SURFACE CELL MATERIALS FOR 9000 MW/YEAR (PEAK).

Material End Product	Use	Thickness (microns)	Overall Process Yield (%)	Amount Required (metric tons)
Copper	Positive Electrode	10	84	22,000
Copper	Negative Collector	10	84	3,780
			Total Copper	26,415
Lead	Positive Electrode Coating	0.5	84	1,440
Inconel	Negative Contact	0.4	84	110
CdS	Semiconductor	3	80	5,020
Cu_2S	Barrier	1	80	4,140
Stannous Oxide	Negative Electrode	0.4	40	1,860
SiO_2	Cover	300	60	300,100

TABLE 14. POWER REQUIREMENTS FOR ANNUAL PRODUCTION OF 9000 MW (PEAK) OF CdS SOLAR CELLS

	Power (MW)
Copper	107[a]
Glass	1[a]
Zinc	4[a]
CdS	1960[aa]
Cu_2S	792[†]
Other Process Power	1000[††]
Total	3864

[a]Calculated from material production energies given in Ref. 77 and yield percent in Table 13.

[aa]Calculated from Figure 9.

[†]Estimated based on relative thickness of Cu_2S to CdS.

[††]Author's estimate.

ENVIRONMENTAL SUMMARY

None of the proposed CdS cell large-scale production concepts have progressed beyond the laboratory stage. Process formulations and quantities are proprietary which limits the evaluation of potential environmental effects. Without precise quantification and accuracy, however, discharge estimates can be made.

Estimates of the emission and effluents resulting from the annual production of solar cells with a generating capacity of 9000 MW/yr (peak) are shown in Table 15. These emissions are derived from Tables 11, 12 and 13 and Figure 9 and include both primary and secondary (off-site) emissions. Emissions from the upstream processing of cadmium-rich fumes[§] and primary emissions[§§] from cell-spray or cell-vacuum processing, however, are not considered.

In order to assess this level of emissions, Table 15 lists the emissions as a percentage of those emitted from the generation of 9000 MW of electrical power by conventional coal-fired utility boilers (see Table 8).

[§]These emissions will exist regardless of the by-product usage of the fumes.

[§§]Inadequate data are available on process emissions (species or rates).

TABLE 15. PRIMARY AND SECONDARY POLLUTANTS[a] GENERATED FROM THE MANUFACTURE OF CADMIUM SULFIDE CELLS FOR 9000 MW/YEAR (PEAK)[b].

	Front Surface Cells		Back Surface Cells	
Pollutants	kg/yr	%[f]	kg/yr	%[f]
Air				
SO_2	6.9×10^6	2.4	7.6×10^6	2.7
Particulates	9.3×10^4	0.4	6.0×10^5	2.5
CO	0.4	Nil	0.5	Nil
Hydrocarbons	0.1	Nil	0.1	Nil
NO_2	1.2	Nil	1.5	Nil
Cd	5.2×10^2	120	6.3×10^2	146
Water				
TSS	6.4×10^3	0.1	2.5×10^5	41.1
Oil/Grease	3.6×10^3	1.8	5.0×10^5	164.4
As	5.5×10^1	0.04	6.1	Nil
Cd	1.1×10^2	1.1	1.3×10^2	1.3
Cu	1.4×10^1	3.9	1.5×10^1	4.2
P	2.0×10^2	0.1	1.8×10^4	9.1
Pb	—	—	0.6	Nil
Se	5.2×10^1	0.1	3.1×10^1	0.1
Zn	5.2×10^1	0.1	3.6×10^1	0.1
Solids				
CdO	1.6×10^2		1.9×10^2	
$ZnSO_4$	1.6×10^2		2.0×10^2	

[a] Excluding emissions from the raw cadmium feedstock (densified, cadmium-rich fumes from zinc smelters) and primary emissions from cell surface processing.

[b] Equivalent to the production of 8820 MT of CdS for front surface cells and 7344 MT of CdS for back surface cells. This represents the demand, in the year 2000, from solar photovoltaic power plants producing 1% of the total U.S. demand for electricity (9000 MW).

[f] Emission as percentage of the corresponding rates emitted from coal-fired steam generators producing 9000 MW/yr of electricity in the year 2000, assuming application of NSPS control technology (see Table 8).

Examination of Table 15 indicates that on a gross, national scale, only the atmospheric emission of cadmium particulates is a significant primary pollution problem in CdS solar cells. The large suspended solids, oil and grease effluent discharges are potentially severe secondary pollution problems if the "back surface" cells are produced. These effluents are generated in the production of the large quantities of glass needed for the "back surface" cells.

In addition to the gross national output of pollutants discussed above and in Table 15, the quantities of heavy metals generated in the production of CdS cells may create locally severe impacts. A synopsis of the toxic effects of arsenic, cadmium, copper, phosphorus, lead, selenium and zinc compounds is given in Appendix D. Because of its potentially severe local impact, a more detailed description of cadmium's properties and toxic effects is given in Appendix E.

Micro-organisms can convert these heavy metals into biologically active compounds by means of oxidative and reductive reactions catalyzed by enzymes. For example, arsenic compounds are reduced and methylated by anaerobes to give dimethylarsine and trimethyl arsine as volatile products of extreme toxicity (Ref. 78). A classification of the heavy metals and other elements according to their susceptibility toward biological activity is shown in Table 16. As indicated in that table, As, Cu, Cd, Pb, Se and Zn (all CdS solar cell effluents) are all in the most acute category.

TABLE 16. TOXICITY AND BIOLOGICAL ACTIVITY[a] OF SELECTED ELEMENTS (REF. 78).

Noncritical	Very Toxic and Easily Accessible	Toxic but Very Insoluble or Very Rare
Al	As	Ga
Br	Cu	Ti
C	Cd	Zr
Fe	Cr	
K	Ni	
P	Pb	
Si	Se	
S	Sn	
	Zn	

[a]Relative tendency toward bioaccumulation and interaction.

The severe toxicity of these metals indicates that careful attention should be given to their control at every significant source in the process. More specific suggestions on control technology needs must await more quantitative process designs and/or detailed environmental impact assessments.

Currently, best available control technology for atmospheric trace metal particulate matter is considered to be electrostatic precipitators, but fine particulates are not controlled adequately by this method (Refs. 59 and 67). Fine particulates (<8 microns) are expected to be a significant fraction of the expected cadmium emissions to the atmosphere (Ref. 60).

The best "wastewater treatment" for heavy metals is zero discharge, because heavy metals are toxic to micro-organisms in low concentrations and must be removed before the wastewater can be subjected to secondary treatment by biological oxidation. Removal of heavy metals from wastewater has been successfully accomplished for many years in the metal plating and finishing industry (Refs. 79 and 80), and this technology may be applied to the solar cell industry. Heavy ion removal from wastewater consists of precipitation with lime. Extensive studies on the toxic effects of heavy metals on biological waste treatment systems were conducted by the Robert A. Taft Sanitary Engineering Center (Ref. 81) and reviewed by Richard Jones (Ref. 82) and this continues to be an active subject of research even today.

Some other potential pollutants from front and back surface processes which are not presently quantifiable are:

- Copper Acetate
- N, N, Dimethyl Thiourea
- Hydrochloric Acid
- Hydrocyanic Acid
- Chromic Acid
- Nitric Acid
- Sulfuric Acid
- Vapor Degreasing Solvents (Halocarbons)

IMPACTS ON NATURAL RESOURCES

U.S. production of cadmium has declined from 1768 tons in 1972 to 1994 tons in 1975 (Ref. 83). This trend may be reversed as a consequence of better controls on zinc processing, and increased awareness of environmental hazards of cadmium. The following excerpt from Ref. 71 describes the complementary roles of increased cadmium production as a consequence of better controls on zinc processing.

"Trends in the Primary Zinc Industry:

> Two trends are evident in the production of primary zinc. First is the dramatic reduction in the domestic zinc production level over the last 20 years, and the second is the rapid phase-out of older pyrometallurgical smelters in favor of electrolytic plants. Both of these trends are of course, directly beneficial in reducing the quantity of cadmium emitted to the air from U.S. zinc smelting operations. A side benefit of the worldwide switching from retorting to electrolytic

zinc is that much less cadmium is being dissipated to consumers as an impurity in zinc. Since the trend is toward less cadmium loss to the environment and less cadmium dissipated in the zinc products, the result is that more recoverable cadmium is becoming available for the primary cadmium industry. Compared to a ratio of cadmium to zinc in ore of 0.5%, the following ratios [Table 17] of primary cadmium production to primary zinc production indicate that the maximum ratio is being approached:"

The 6000 tons required for the production of solar cells will not significantly deplete the reserves which are estimated to be 164 thousand tons. The recovery of cadmium is dependent, however, on zinc production, with an estimated recovery of 5 kg cadmium per ton of contained zinc in zinc reserves. The projected annual demand for zinc in the year 2000 ranges from 1.7 to 3.1 x 10^6 tons (Ref. 84). Maximum cadmium production would therefore approximate 16500 tons. Thus the cadmium demand from CdS solar cells would represent 36% of the market and would exert appreciable upward pressures on cadmium prices. Solar cell demand, however, could probably be met.

TABLE 17. RELATIONS BETWEEN CADMIUM AND ZINC PRODUCTION IN THE 20TH CENTURY (REF. 71)

Years	Ratio of Cadmium Production to Zinc Production (%)
1901-10	0.002
1910-20	0.009
1920-30	0.056
1930-40	0.17
1940-50	0.25
1950-60	0.27
1960-68	0.33

Quantities of other materials required for production of CdS are not expected to impact resource availability (Ref. 84).

POLLUTION CONTROL TECHNOLOGY READINESS AND PROJECTIONS

Complete definition of the environmental considerations awaits development of production processes beyond the current paper study/laboratory sample level. However, current pollution control practices utilized in the zinc and lead mining, smelting, and refining industries should yield 90% or better control of cadmium losses from the incoming feedstock during the production of CdS. Application of control techniques recommended in Effluent Limitation Guidelines and New Source Performance Standards, for the lead and zinc industries (Ref. 57) should adequately control emissions other than cadmium.

Although CdS is fairly stable the potential reactivity of Cu_2S dictates that cell disposal, after electrical generating lifetime, must be controlled. The instability of Cu_2S may be the cause of the short lifetimes that most CdS cells have experienced. The possibility of slow erosion and dissolution of discarded CdS needs to be evaluated as well as the feasibility of reclamation.

SECTION 6

GALLIUM ARSENIDE PROCESS

GENERAL PROCESS DESCRIPTION

GaAs Process Description

A hypothetical process has been synthesized based on Refs. 89 and 90 and informal communications with Alcoa and Eagle-Picher personnel. The process flow diagram, material balance and power requirements based on 100 MW/yr of solar cell production are presented in Figures 14, 15 and 16.

Gallium Production and Purification--

Gallium is produced as a byproduct of the extraction of aluminum from bauxite.

Caustic is used to extract sodium aluminate from bauxite in the manufacture of aluminum. The aluminate is precipitated and the spent caustic solution is recirculated for further bauxite extraction. Recirculation of the caustic solution allows a buildup of gallate concentration to an Al/Ga ratio of approximately 500/1. This solution is the starting point for gallium refining.

The bulk of the aluminate is fractionally precipitated by neutralizing the caustic solution by bubbling carbon dioxide through it. The precipitate is recycled to the alumina process and the filtrate is further treated with carbon dioxide to precipitate the gallate with the balance of the aluminate. Leaching of the precipitate with sodium hydroxide yields a gallate-rich solution from which gallium can be electrolytically deposited. 99.5% pure gallium, in the liquid phase, is collected. Proprietary chemical processes are used to further refine the gallium to up to 99.999% purity.

The chemical reactions for the processes are:

Aluminum Precipitator:

$$Na_2Al_2O_4 + 2\ NaOH + 2\ CO_2 + 3\ H_2O \rightarrow 2\ Na_2CO_3 + Al_2O_3 \cdot 3\ H_2O$$

Gallate Precipitator:

$$2\ NaH_2GaO_3 + CO_2 + H_2O \rightarrow 2\ Ga(OH)_3 + Na_2CO_3$$

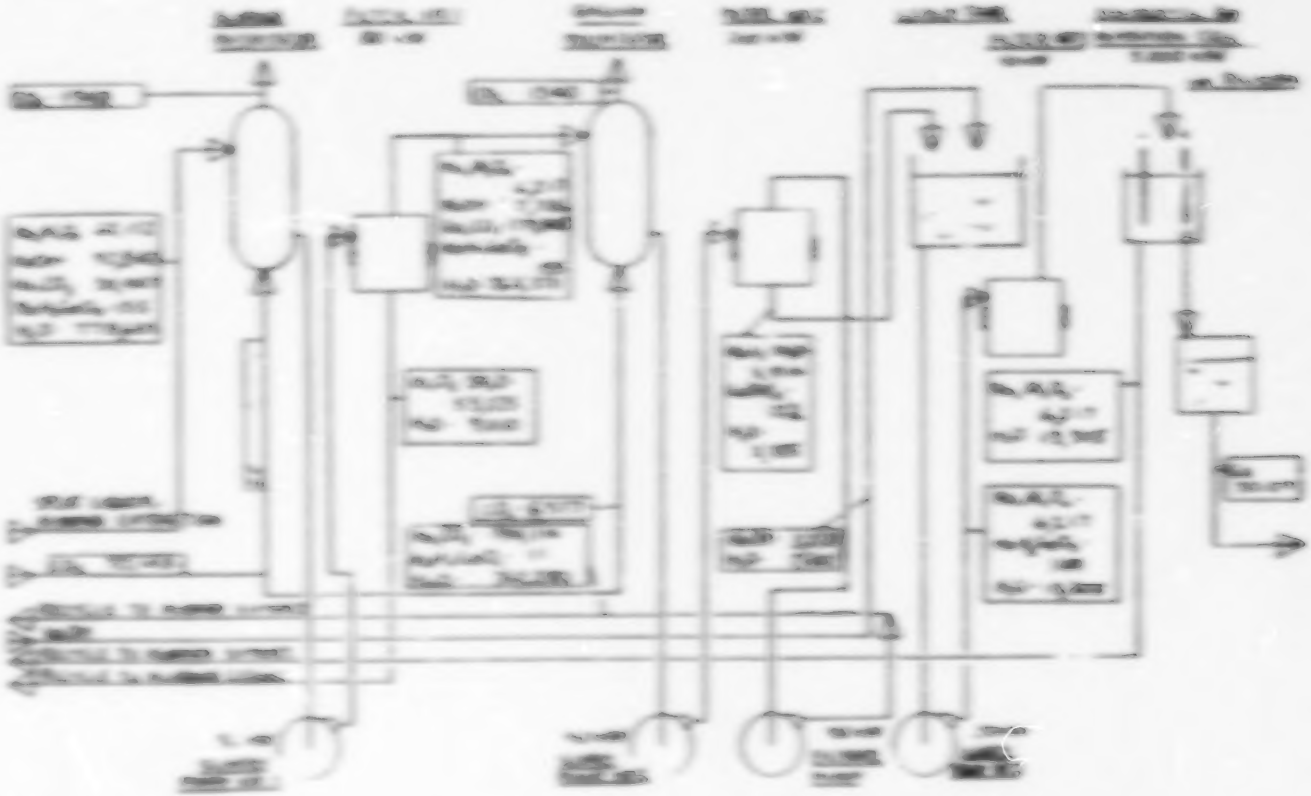


Figure 14. Process flow diagram -- Co.

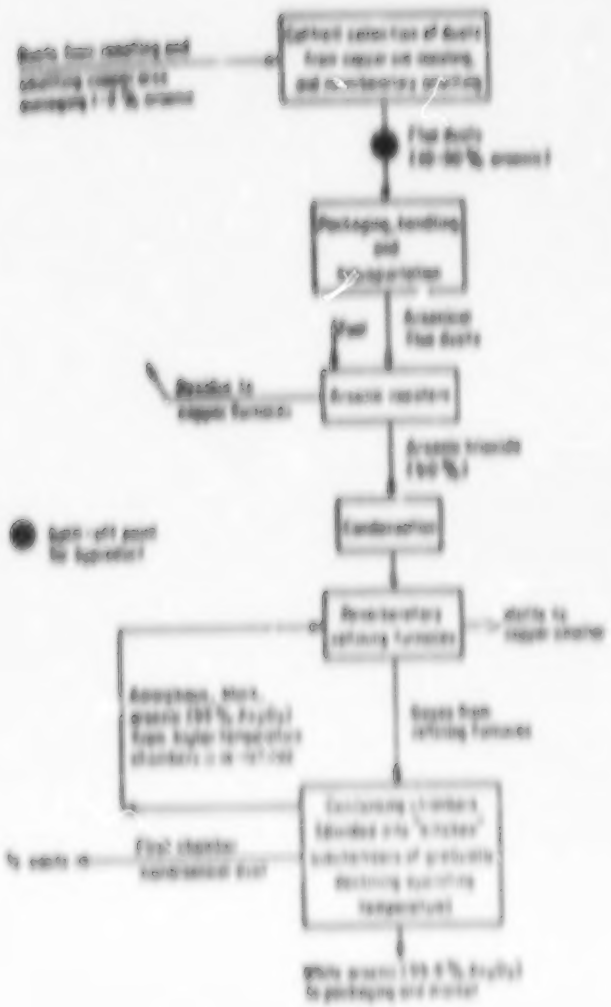


Figure 15. Arsenic production from flue dusts (Ref. 91).

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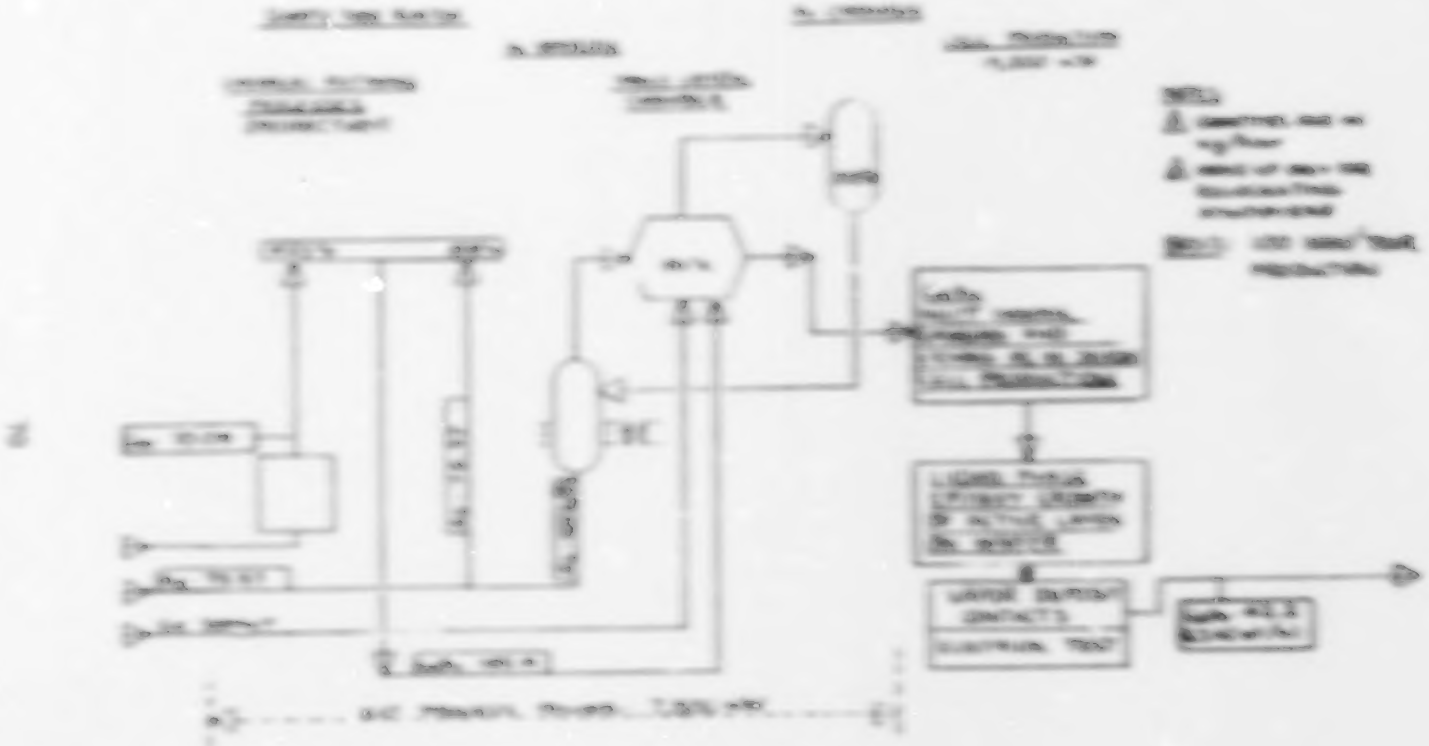

Figure 14. Process flow diagram -- Co to CoAs cell.

Leach Tank:

$$Al_2O_3 + 3\,H_2O + 2\,NaOH \rightarrow Na_2Al_2O_4 + 4\,H_2O$$

$$Ga(OH)_3 + NaOH \rightarrow NaH_2GaO_3 + H_2O$$

Consult Figure 14.

Arsenic Production and Purification

Arsenic is produced in oxide form as a byproduct mainly from treatment of the arsenic bearing flue dusts collected from the smelting of such metals as copper and lead (Figure 15).

The flue dusts of 10 to 30% arsenic content from the smelters are roasted at 400 C followed by a condensation step to produce crude trioxide of 90 to 95% purity. The crude oxide is vaporized in reverberatory furnaces at a roasting temperature of 550 C and the refined arsenic trioxide of 94.9% purity is obtained as the lower temperature fraction in condensing chambers consisting of a series of kitchens of gradually declining operating temperature. The nonarsenical dust from the first chamber is roasted and the higher temperature fraction is re-refined. The refining furnace residue containing about 20% of the crude oxide charge to the furnace is recycled to the smelting operation.

Metallic arsenic can be obtained by thermal reduction of the refined trioxide with charcoal in a cylindrical retort and by condensing the metallic vapor (Ref. 92).

At present, all domestic arsenic is produced at one mill: American Smelting and Refining Co., Tacoma, Washington. Imports account for about 75% of U.S. requirements (Ref. 29). An increase of 35% in imports would meet projected needs.

GaAs Compounding (Fig. 16):

High purity (six 9's) gallium and arsenic are compounded inside an evacuated quartz bottle. The relative quantity of arsenic to gallium is slightly below stoichiometric to minimize residual arsenic when the quartz bottle is opened. The gallium and arsenic are heated independently within the bottle and caused to react. Some of the arsenic reacts with the SiO_2 inside the bottle. The products when the bottle is opened are:

1. GaAs
2. Some gallium which is reused
3. The quartz bottle with some arsenic contamination on the inner wall.

Part of the quartz bottle is removed. The other part is etched with HF-HNO_3 to remove the arsenic and then it is reused. The amounts cannot be determined at present due to the proprietary nature of this process. Safe

handling and disposal will have to be determined after quantities are established; further environmental study is warranted.

The high purity, polycrystalline GaAs proceeds to a single crystal growing chamber.

Currently the bulk of n-type GaAs used for solar cells is made from single crystals produced by a modified horizontal Bridgman process (Ref. 93), from melted (1510 K) GaAs and the dopant. This process produces dislocation-free n-type GaAs crystals which have been doped with germanium. During growth, which is started in vacuum, arsenic vapor pressure is carefully controlled to maintain stoichiometric growth.

The use of quartz as a container for gallium and molten GaAs, and as a reaction vessel in which GaAs synthesis is carried out, may lead to Si contamination of the GaAs grown in these containers. Si can act as an electron donor or an acceptor and must be restricted to maintain electronic properties. Incorporation of Si at a level of a fraction of a part per million can have a serious effect on the electrical behavior. To suppress such contamination a small diameter tube connects the arsenic reservoir with the boat in which the GaAs crystal is grown. A large temperature gradient is maintained over a portion of this tube to suppress the transport of Ga_2O. This substance, in the vapor phase at GaAs melt temperatures, is formed by the reaction of gallium with SiO_2 in the boat containing the charge. Free Si is also produced, which can be incorporated into the growing crystal. Maintaining a high concentration of Ga_2O vapor suppresses the reaction. This method produces high purity n-type GaAs. Further details of this process are proprietary.

Preparation of n GaAs Single Crystal for Cell Fabrication--

After the bulk n-type single crystal of GaAs is grown it is cleaned and sliced into 0.125 mm wafers. The slicing is usually done by reciprocating multiple band saws; but it is also done with water-cooled diamond saws. GaAs is much more fragile than Si; and this limits the thinness of wafers. The kerf material is separated from cutting grit and is recycled by the gallium producer. After slicing, the wafers are cleaned with sulfuric acid and H_2O_2.

Although the resulting wafer is of high purity and good crystal, it has poor diffusion lengths which lower the response to long wavelength light. This deficiency is overcome by epitaxially depositing a layer of n-type GaAs which has good diffusion lengths onto the wafer. This layer then becomes the base on which p-type (zinc doped) GaAlAs is grown (Ref. 94).

The liquid phase epitaxial (LPE) growth of the good-diffusion-length GaAs on the GaAs substrate takes place in a vacuum. In a graphite boat, which has been baked several hours in vacuum at 1073 K n-doped GaAs is soaked for two hours with palladium diffused H_2 at 1120 K. The melt is brought into contact with the heated GaAs substrate (wafer). The temperature of the system is then reduced at a controlled rate and the GaAs crystallizes from the melt onto the substrate (Ref. 93).

This is followed by a similar LPE growth of 1 micron of zinc doped AlGaAs. The zinc dopant diffuses into the n-type LPE GaAs layer producing the p-n junction below a thin p-type layer. The resulting GaAs-AlGaAs heterojunction confines electrons generated in the p-type GaAs layer giving low surface recombination velocity which increases efficiency over a straight GaAs cell (Ref. 95).

The 1 micron thick AlGaAs is a transparent conductive coating which permits reduction of surface resistance and the corresponding series resistance of the cell without excessive doping (Ref. 96). This layer thickness could be reduced to 0.3 micron to minimize optical losses and improve cell efficiency (Ref. 93).

Contact Application--

The front contact and grid as well as the back contact are formed by vapor deposition.

Anti-Reflective Coating--

Anti-reflective coatings are required for high performance. The optimum A/R material has not been selected. The cross section of a GaAs cell is shown in Figure 17.

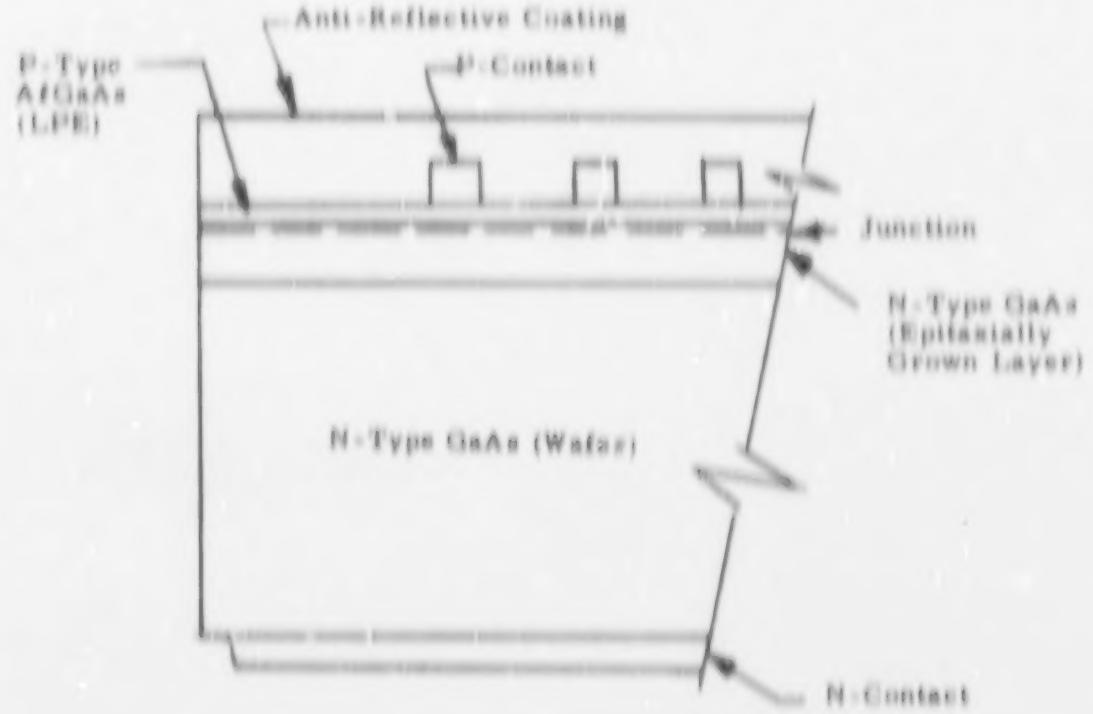

Figure 17. Cross-section of GaAs cell.

GaAs PROCESS MATERIAL REQUIREMENTS (REFS. 89, 97-98)

Consumption and production are summarized in Table 18 based on annual solar cell production to generate 4500 MW of peak power and the process described previously.

Presently, GaAs cells are produced in very low volume using laboratory equipment. One producer is installing equipment which will produce larger cells but this is still of a laboratory nature.

The yields for material processing for GaAs are expected to approximate those obtained with Si. This is justified by the fact that with the exception of the liquid phase epitaxial growth steps, the processes involved in cell justification are similar.

The yields assumed for this study are listed in Table 19.

Using 125 micron cell thickness, 5.32 specific gravity and 29% cell yield from polycrystalline GaAs, a cell area to weight ratio of 0.43 m^2/kg is calculated. An assumed efficiency of 18% yields 0.078 kW (peak power) per kilogram of GaAs.

From the assumed life of 10 years, we determine that arrays with 4500 MW (peak output) must be produced each year to generate 1% of year 2000 generating capacity. This is the same result we obtained for Si, but only half the production required of CdS cells.

A "single" manufacturing facility producing only 100 MW/yr of GaAs solar cells, which corresponds to the same capacity Si cell facility, would have 1.271×10^6 kg/yr of pure polycrystalline GaAs going into cell production.

The gallium is shown to be recovered from the spent caustic liquor from the alumina extraction process. The quantities to be processed are large which raises the question of availability of materials. Gallium occurs in bauxite and averages 0.005% in sphalerite from the tri-state area of Kansas, Missouri and Oklahoma. This means that over 1×10^9 metric tons of bauxite would have to be processed each year to get enough gallium for the above production. Another approach is to look at the world reserves of gallium with respect to the above requirements. Reference 89 estimates our domestic gallium reserves at 2.7×10^6 kg. Estimated consumption from Figure 12 is 2.28×10^6 kg/yr. Obviously, it cannot be done as conceived.

A practical approach using GaAs would require at least a 100 to 1 concentration of solar energy to reduce consumption of gallium to less than 1% of projected available domestic resources. Worldwide resources of gallium may alleviate the demand-supply problem, but this demand would strain the industry and impact cost.

The arsenic required would be no problem compared to gallium. The required quantity based on a 100:1 solar concentration factor is only about 0.25% of the U.S. annual imports of arsenic (Ref. 97).

TABLE 18. GaAs PROCESS MATERIAL CONSUMPTION AND PRODUCTION SUMMARY FOR 4500 MW

Raw Materials	Quantity, 10^3 MT	Products and Wastes	Quantity, 10^3 MT
Solids:		Solids:	
As, High Purity	0.296	GaAs Solar Cells (as Ga, 0.08)	0.166
Germanium	0.1-0.02	$Al_2O_3 \cdot 3H_2O$	209.
Zn	trace	H_2O	35.5
Spent Liquor-Alumina Extraction:		Liquors Recycled to Alumina Process:	
$Na_2Al_2O_4$	248.		
NaOH	166.	$Na_2Al_2O_4$	24.5
Na_2CO_3	122.	NaH_2GaO_3	0
NaH_2GaO_3	0.607	Na_2CO_3	17.6
(as Ga, 0.297)		H_2O	3059
H_2O	3059.	Gases:	
Caustic:		CO_2	12.98
NaOH	12.13	Cutting and Grinding	
H_2O	30.32	Slurry for Reclamation:	
Gases:		Abrasive Grit	0.89
CO_2	277.	GaAs (as Ga, 0.196)	0.406
Cutting and Grinding		Vehicle	0.89
Abrasive Grit	0.89	Cutting and Grinding Sludge-Discarded:	
Clay	0.89	Clay	0.89
Slurry Vehicle	0.89	Worn Blades	0.26
Saw Blades	0.26	Mounting Cement	0.02
Mounting Cement	0.02	Mounting Blocks	0.16
Mounting Blocks	0.16	Lubricants	0.09
Lubricants	0.09	Quartz Waste	0.01
Quartz Reactor Tubes	0.01		

TABLE 19. GaAs YIELDS IN CELL PRODUCTION

Item	Net Percent of Polycrystalline	Process Yield (%)
GaAs as Compounded	100	--
GaAs Crystal Yield	90	90
Wafer Yield	40	45
Cell Fabrication Yield	32	80
Electrical Cell Yield	29	90

Concentration of incident solar energy for use with GaAs cells has been discussed by James and Moon (Ref. 95) and is judged feasible for very high concentration factors.

Efforts to reduce consumption of GaAs are directed toward a process for liquid phase epitaxial growth of a very thin (i.e., 1 to 3 micron) layer of GaAs on a low cost substrate followed by LPE growth of p-type GaAlAs. Similar efforts are proceeding using chemical vapor deposition (CVD) of the layers. Successful development of either process would reduce GaAs consumption by 96% and, thereby ease the necessity for high concentration factors.

GaAs PROCESS POWER REQUIREMENTS

Table 20 is a summary of power requirements based on a plant annually manufacturing 100 MW (peak power) of GaAs solar cells. The power quantities were collected from Figures 14 and 15 and represent estimates of the major requirements. Based on an average peak power ratio of 5:1, the average output of the 100 MW peak power solar cells would be 100 MW/5 = 20 MW. Energy payback on the cell basis would be 57.98 MW/20MW/year = 2.90 years. Since concentration of solar energy is a probability with GaAs cells, the energy payback should be analysed based on potential concentrator designs.

IMPACT ON NATURAL RESOURCES

Gallium occurs widely in nature, particularly in aluminum bearing minerals. However, because of its very low concentration in even the highest grade ores (0.002 to 0.008%) processing ores simply for their gallium content is not economical. The two current sources for gallium are from aluminum processing and from recycling of mine tailings. British fly ash has been mentioned as a possible source.

The supply of gallium produced from mine tailings may be limited if large quantities are required. The other products of this recycling include zinc rich potassium phosphate which is used by fertilizer manufacturers.

TABLE 20. SUMMARY OF POWER REQUIREMENTS FOR PRODUCTION OF 100 MW/YEAR PEAK POWER GaAs SOLAR CELLS

	Power, kW
Slurry Pump No. 1	150
Slurry Pump No. 2	150
Slurry Pump No. 3	30
Filtrate Pump	150
Filter No. 1	250
Filter No. 2	200
Filter No. 3	50
Gallium Electrodeposition	17,000
Gallium Refining, GaAs Formulation and Single Crystal Growing	25,000
Cell Production	15,000
Total	57,980

sulfur, and acidic sand which is used to neutralize the basic soil in the region of the processing plant. The marketability of these products may limit the availability of gallium from this source.

The probable domestic demand for gallium in the year 2000 is 3.2×10^4 kg, (Ref. 98) not including any allocation for solar cell production. To produce 4500 MW of GaAs solar cells, would require 2.98×10^5 kg, thus increasing demand by one order of magnitude. Clearly, the level of increased production required to meet such demand is not feasible because of the dependence of gallium production on other materials such as aluminum and zinc.

As discussed earlier, large-scale usage of gallium for solar cells is only practical if concentration factors of 100 or greater are used. With no concentration, the estimated (Ref. 98) U.S. reserve of 2.7×10^6 kg of gallium would be expended in meeting approximately 0.1% of the year 2000 U.S. electrical energy requirements.

If gallium comes into greater demand, its cost will surely rise. The above factors suggest that, at present, large-scale use of GaAs is limited to applications where concentrators and/or higher cell costs can be accommodated.

It may become competitive if efforts to reduce material consumption and/or to develop high concentration reflectors are successful. The large

erate use of gallium arsenide solar cells will require both the use of concentrators and the reduction of cell thickness.

ENVIRONMENTAL CONSEQUENCES

The GaAs solar cell production problems which impact the environment are listed in Table 21. The pollution problems associated with arsenic production and handling have not been addressed in this study; and, they are being continuously reviewed by OSHA. Details on GaAs production are limited; and there are probably hazardous chemicals to be disposed of.

TABLE 21. ENVIRONMENTAL CONSEQUENCES AND CORRECTIVE ACTIONS – GaAs

Problem	Action
Arsenic production and handling	Requires further definition of safe limits by OSHA
HF during etching of quartz reactor	Requires quantification and safeguards for personnel
Requirement for Ga exceeds supply	Consider concentrators and alternate Ga conserving cell production methods
Unknown proprietary chemicals used during GaAs compounding and doping and crystal growth	Determine chemicals and identify environmental action required, if any

The technology readiness of environmental aspects of GaAs cell production related primarily to the handling of arsenic and the large amount of process energy required. The extraction of gallium as a byproduct of aluminum production is a "clean" process in that it feeds all residual products back to the aluminum production stream.

One proposed GaAs cell production method involves the use of organometallic materials in a chemical vapor deposition process. Environmental problems posed by using this and other processes must be examined further.

ECONOMIC CONSEQUENCES

Cost is the principal factor limiting wider application of solar panels. However, usual comparisons using common utility costs do not take into account ecological advantages and the ever increasing costs of alternate energy sources, in part due to environmental controls.

In each solar cell system, the cost of raw materials tends to increase with demand, since quality or concentration of mined minerals decreases with consumption.

New process development normally concentrates on making the process work and places environmental aspects in a lower priority. Care must be taken to allocate the development and production costs of environmental control to new processes in any economic analysis.

An economic analysis of the solar cell systems was not accomplished in this study. Costs can be estimated for the process once material requirements are defined, and there is some certainty about which process will be likely to see major industrial application.

In the case of GaAs, complications arise from the probable use of solar concentrators which drastically reduce all requirements, but add a large unknown. System analyses and studies should be conducted to ascertain optical concentration factors and generate feasible design concepts. In a companion report (Ref. 61) we have examined construction materials and dollar requirements for a large concentrator Si photovoltaic utility plant. The support structures and concentrators were found to be the principal cost elements, rather than photovoltaic material.

SECTION 7

ALTERNATE PROCESSES

The processes discussed in preceding sections are considered to have the highest probability for large-scale production; however, other processes are being studied.

One of the major factors affecting the environmental impact of solar cell production is the amount of material in the finished cell. The amount of material required to produce the cells is a function of the production yield. The area of cells produced from supplied material is determined by the relation:

$$\text{Area to mass input } \frac{m^2}{kg} = \frac{\text{production yield}}{\text{cell mass to area } kg/m^2}$$

The peak power-to-mass input (in kilowatts per kilogram) is the product of area-to-mass input and cell efficiency.

Programs to reduce the amount of material, increase yields through the process steps, and increase cell efficiency are all aimed at maximizing material utilization, which, in turn, will reduce environmental problems. A discussion of the potential for some of the current and proposed cell production methods follows.

Several methods to improve utilization of Si in cell production are being studied under ERDA/JPL (Ref. 7) funding. Current production (point 1 in Figure 18) using sliced single crystal Si 0.6 mm thick yields 40 W/m^2 at 10% efficiency per kilogram of polycrystalline Si. This study is based on 1977 projections (Ref. 16) for 14% efficiency cells 0.15 mm thick yielding 1.0 m^2 or 140 W/kg of polycrystalline Si.

The ultimate growth potential for sliced Si wafers is to produce 1.61 m^2 of 14% efficiency cells or 225 W/kg of polycrystalline Si as calculated from Ref. 16.

The most probable alternate Si cell manufacturing method is single crystal ribbons growth from polycrystalline melt by edge-fed growth (EFG). Currently, this method yields less cell area and lower efficiencies than sliced crystals. However, if development efforts are successful, the potential is for slightly higher area yields. From an environmental viewpoint, the principal advantage of this process will be that the waste Si will be in solid form, not in sludge as it is with wafer slicing.

Projected EFG silicon utilisation is for 84 W/kg of polycrystalline Si; ultimate growth potential is for 260 W/kg as calculated from Ref. 12.

A third method of forming Si into cells is to deposit it by chemical vapour deposition (CVD). Efforts to achieve high area utilisation of the Si have been successful; but the efficiencies have been very low, owing to the crystalline formation during deposition. Environmental considerations of large scale production using CVD are not understood since details of the process methods and chemicals and energies are unavailable. The current laboratory samples yield 6.3 m^2/kg of polycrystalline Si at 1.5% efficiency. Clearly, if efforts to improve efficiency are successful, this method will produce the highest material utilisation of the three Si methods.

Zoutendyk (Ref. 99) recently reviewed some R&D directions currently being pursued to develop low-cost cells. Recent progress has brightened hopes that doped amorphous Si may be developed successfully (Ref. 100).

Few GaAs chemical vapour deposition (CVD) and liquid phase epitaxy (LPE) are being studied to improve material utilisation. Efforts to produce cells by growing very thin layers of GaAs either on thin films or on alternate low cost substrates have not been successful; but the work is promising.

The method, discussed in this study, of slicing wafers from single crystals and growing junction layers by LPE produces 0.42 m^2 of cells (76 W/kg) of polycrystalline GaAs, based on 18% efficiency.

Further increases in output using this method are not expected due to losses during slicing which are similar to those in Si cell production.

Currently, proposed CdS cells already utilise very thin (1 to 5 micron) layers of active material. Alternate production methods are aimed at improving cell life and efficiency rather than material improvement.

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Appendix A

ATMOSPHERIC EMISSION FACTORS FOR RAW MATERIALS EXTRACTION AND PRODUCTION

Emission factors appearing in the following tables appeared originally in the references cited, in units conventional to their respective industries. They have been converted into kilogram (kg) pollutant per metric ton (MT) of final photovoltaic cell material, for example, kg (SO_x)/MT(Si). To determine the total emission of a specific pollutant, the sum of all emission factors (including unit operations for which we have no data) would be multiplied by the total quantity of photovoltaic solar cell material in metric tons.

TABLE A-1. EMISSION FACTORS FOR QUARTZITE MINING UNIT OPERATIONS* (DERIVED FROM REF. 43).

Unit Operations	kg/MT (of Material Processed Through Crusher)	kg/MT (of Solar Cell Silicon)**
Drilling	0.030	1.64
Blasting	†	†
Loading at Quarry and Vehicular Transport to Plant	0.170	9.32
Unloading and Primary Crushing and Screening	††	††
Secondary Crushing and Screening	0.012	0.66
Conveying	†	†
Unloading at Stockpile	†	†
Wind Erosion of Stockpiles Unpaved Road Traffic Between Finished Stockpile and Nearest Paved Highway	†	†
Total (± 95% Confidence Interval)	0.212 (± 0.100)	11.62 (± 5.48)
Fraction Respirable, by Weight	6%	6%

*No NO_x or SO_x (products of explosives combustion) were detected outside the plant perimeter.

**Using ratio 54.8 kg 98% SiO_2 required to produce 1 kg solar cell Si.

†Negligible, i.e., less than 1% of total.

††Only wet screening and washing procedure was used at the quartzite plant and there was no primary crusher.

TABLE A-2. ELEMENTAL ANALYSIS OF EMISSIONS FROM QUARTZITE PROCESSING (DERIVED FROM REF. 23).

Element	Weight %
Mn	0.03 - 0.04
Fe	0.5 - 5.5
Cu	0.4 - 2.0
Zn	<1.06
Pb	0.16 - 0.4
Na	0.2 - 0.53
Mg	0.1 - 0.2
Al	0.4 - 1.3
Ti	0.03 - 0.07
V	<0.005
Cr	0.01 - 0.02
Si	3.3 - 20
Ca	1.2 - 6.6
Sn	0.01 - 0.02
Ni	<0.02
Ag	<0.006

TABLE A-1. [illegible]

Pollutant	Occ. Underlying	Equivalent Emission Factor (kg Pollutant per MG Silicon Cut): Si-Product, Sand Dross, Wet Gaseous Cutting — No Controls								
		Overcut	Cutting	Discharging (Pushing)[a]	Wet Quenching	Underfiring	Complete Cycle	Battery Dross (No Controls)	Sublation, Sand Dross, Wet Gaseous Cutting — with Controls — Complete Cycle	Dry Gaseous Cutting — Quenching Skin
Total Emissions	High	—	—	—	—	—	(Note A)	0.03	(Note A)	0.1–32
Particulate, Suspended	4.2	30.1	1.1	6.4	15.6	—	—	2.6	—	—
SO_2	50	0.03–0.09	—	—	—	42.8	—	High	0.9	—
CO		6.5	1.6	0.8	—	—	150.0	10.7	1.0	—
Total Hydrocarbs		26.8	30.1	2.1	—	—	—	65.4	—	—
Aromatic Hydrocarbs		—	—	—	—	—	4.7	—	0.8	—
Benzene Hydrocarbs		2.4	2.4	2.4	—	—	—	—	—	—
NO_x		0.3–18.0	—	—	—	—	—	—	—	—
SO_2		0.2	1.1	1.1	—	—	3.0	21.4	0.3	—
H_2S		13.8	—	—	—	—	2.8	High	4.8	—
Cyanides as HCN		1.0	—	—	—	—	30.1	—	1.1	—
Zinc		1.2	—	—	—	—	—	—	—	—
Phenols		—	—	—	—	—	2.6	High	0.4	—
Particle Dross		—	—	—	—	—	0.4	High	0.05+	—

Note A: Based only upon operations for which there are published values, since [illegible] emissions for byproduct cutting, which are upwards [illegible] 30 kg MC in [illegible] or less, and 20 kg MC in [illegible] cases.

TABLE A-4. COAL EMISSION FACTORS FOR ATMOSPHERIC PARTICULATES (REF. 39).

Source Type	Emission Factor kg/MT Coal	kg/MT Solar Cell**
Surface Coal Mining	12.5×10^{-3}	0.375
Drilling	1.6×10^{-3}	0.048
Coal Loading	1.7×10^{-3}	0.051
Transport and Unloading	4.9×10^{-3}	0.147
Blasting	4.2×10^{-3}	0.126
Total	24.9×10^{-3}	0.747
Auger Mining	0.8×10^{-3}	0.024
Coal Storage	6.5×10^{-3}	0.195

*Total suspended respirable particulate (< 7 μm).

**Using the ratio 30 kg coal/kg solar cell Si.

Appendix B

GLOSSARY

Symbol	Description
AM0	Air mass zero (extraterrestrial solar spectral irradiance value) = 1353 W/m^2
AM1	Air mass one (direct solar spectral irradiance at ground level) = 956 W/m^2
Average Power	Power output integrated over 24 hours and divided by 24
BATEA	"Best available technology economically achievable"
BOD	Biochemical oxygen demand
BPCTCA	"Best practicable control technology currently available"
Capacity Factor	Ratio of actual output to maximum design output
CFR	Code of Federal Regulations
COD	Chemical oxygen demand
CVD	Chemical vapor deposition
DSCF	Dry standard cubic feet
DSCFM	Dry standard cubic feet per minute
DSCM	Dry standard cubic meters
DSCMM	Dry standard cubic meters per minute
Efficiency	$100 \cdot \frac{\text{Peak Power Output}}{\text{Incident Energy at AM1}}$
EFG	Edge-fed film growth
ELG	Effluent Limitations Guideline(s)
EPA	Environmental Protection Agency
ERDA	Energy Research and Development Admin.
ESP	Electrostatic precipitator
FR	Federal Register
GE	General Electric Company
HC	Hydrocarbon

Symbol	Description
Insolation	Actual irradiance for given geometry, altitude location and meteorological conditions
IR	Infrared
JPL	Jet Propulsion Laboratory
LD_{Lo}	Lethal dose low
LD_{50}	Lethal dose – 50%
MT	Metric ton (Not megaton); 1000 kg
MW	Megawatt
NIOSH	National Institute of Occupational Safety and Health
NO_x	Nitrogen oxides
NPDES	National Pollutant Discharge Elimination System
NSPS	New Source Performance Standard(s)
OSHA	Occupational Safety and Health Administration
Packing Factor	Solar cell area as percent of total solar array area
Peak Power	Power output at solar noon under optimal meteorological conditions with solar radiation at normal incidence
Q	Quad = 10^{15} Btu
Respirable Particulate	Atmospheric particle (aerosol) small enough to be inhaled into the lungs. Often taken to mean $\leq 7\ \mu m$
R&D	Research and development
Scf	Standard cubic feet
Scfm	Standard cubic feet per minute
Scm	Standard cubic meter
Settleable Particulate	An atmospheric particle so large that it does not remain suspended. Often taken to mean $\geq 50\ \mu m$
SO_x	Sulfur oxides
Suspended Particulate	Any atmospheric particle small enough to remain airborne
TC_{Lo}	Toxic concentration low

Symbol	Description
TDLo	Toxic dose low
TFX	Toxic effects
THC	Total hydrocarbon
TLV	Threshold lethal value
TSS	Total suspended solids
TWA	Time weighted average
TXDB	Qualifying toxic dose
UV	Ultraviolet.

Appendix C
CONVERSION FACTORS

Mass	μg	g	MT	lb	Short Ton
1 μg =	1	10^{-6}	10^{-12}	2.205×10^{-9}	1.102×10^{-12}
1 g =	10^{6}	1	0.001	2.205	1.102×10^{-3}
1 MT =	10^{12}	10^{3}	1	2205	1.102
1 lb =	4.536×10^{8}	0.4536	4.536×10^{-4}	1	5×10^{-4}
1 Short Ton =	9.074×10^{11}	90.74	0.9074	2000	1

Length	cm	m	in.	ft	mi
1 cm =	1	0.01	0.3937	0.03281	6.214×10^{-6}
1 m =	100	1	39.37	3.281	6.214×10^{-4}
1 in. =	2.540	0.02540	1	0.08333	1.578×10^{-5}
1 ft =	30.48	0.3048	12	1	1.645×10^{-4}
1 mi =	1.609×10^{5}	1609	63360	5280	1

Area	m^2	hectare	ft^2	acre	mi^2
1 m^2 =	1	10^{-4}	10.76	2.471×10^{-4}	3.861×10^{-7}
1 hectare =	10^{4}	1	1.076×10^{5}	2.471	3.861×10^{-3}
1 ft^2 =	0.09290	9.290×10^{-6}	1	2.296×10^{-5}	3.587×10^{-8}
1 acre =	4047	0.4047	43560	1	1.563×10^{-3}
1 mi^2 =	2.590×10^{6}	259.0	2.788×10^{7}	640	1

Volume	l	m^3	gal	ft^3
1 l =	1	0.001	0.2642	0.0353
1 m^3 =	1000	1	264.2	35.31
1 gal =	3.785	3.785×10^{-3}	1	0.1337
1 ft^3 =	28.32	0.02832	7.481	1

Pressure	N/m^2	psi
1 N/m^2 =	1	1.450×10^{-4}
1 psi =	6895	1

Energy	kWh	kcal	Joule	Btu
1 kWh =	1	859.8	3.6×10^{6}	3414
1 kcal =	1.162×10^{-3}	1	4184	3.968
1 Joule =	2.778×10^{-7}	2.387×10^{-4}	1	9.483×10^{-4}
1 Btu =	2.929×10^{-4}	0.2520	1054	1

Power	kW	Btu/hr
1 kW =	1	3414
1 Btu/hr =	2.929×10^{-4}	1

Concentration[a] in Air	$\mu g/m^3$	ppm (Vol.)	ppm (Wt)	lb/ft^3
1 $\mu g/m^3$ (μg/scm)	1	0.0380/M	0.347×10^{-6}	6.243×10^{-11}
1 ppm (Vol., 1958)	M/0.02404	1	M/28.8	M/1.551×10^{9}
1 ppm (Wt)	1.178×10^{3}	28.8/M	1	7.48×10^{-5}
1 lb/ft^3 (lb/scf)	1.602×10^{10}	3.857×10^{8}/M	1.337×10^{5}	1

[a] M = molecular weight.

CONVERSION FACTORS
MASS DISCHARGE OR EMISSION RATES
(From Robert A. Taft Center "Handbook of Air Pollution")

Given units \ Desired units	g/sec	g/min	kg/hr	kg/day	lbs/min	lbs/hr	lbs/day	tons/hr	tons/day	tons/yr
g/sec	1.0	60.0	3.6	8.640 x 10	1.3228 x 10^{-1}	7.9367	1.9048 x 10^{2}	3.9683 x 10^{-3}	9.5240 x 10^{-2}	3.4743 x 10
g/min	1.6667 x 10^{-2}	1.0	6.0 x 10^{-2}	1.4400	2.2046 x 10^{-3}	1.3228 x 10^{-1}	3.1747	6.6139 x 10^{-5}	1.5873 x 10^{-3}	5.7908 x 10^{-1}
kg/hr	2.7778 x 10^{-1}	16.667	1.0	2.4000 x 10	3.6744 x 10^{-2}	2.2046	5.2911 x 10	1.1023 x 10^{-3}	2.6456 x 10^{-2}	9.6491
kg/day	1.1574 x 10^{-2}	6.9444 x 10^{-1}	4.1667 x 10^{-2}	1.0	1.5310 x 10^{-3}	9.1860 x 10^{-2}	2.2046	4.5930 x 10^{-5}	1.1023 x 10^{-3}	4.0203 x 10^{-1}
lbs/min	7.5599	4.5359 x 10^{2}	2.7215 x 10	6.5317 x 10^{2}	1.0	60.0	1.44 x 10^{3}	3.000 x 10^{-2}	7.2000 x 10^{-1}	2.6280 x 10^{2}
lbs/hr	1.2600 x 10^{-1}	7.5599	4.5359 x 10^{-1}	1.0881 x 10	1.6667 x 10^{-2}	1.0	24.0	5.0000 x 10^{-4}	1.2000 x 10^{-2}	4.3800
lbs/day	5.2499 x 10^{-3}	3.1499 x 10^{-1}	1.8900 x 10^{-2}	4.5359 x 10^{-1}	6.9444 x 10^{-4}	4.1667 x 10^{-2}	1.0	2.0833 x 10^{-5}	5.0000 x 10^{-4}	1.8250 x 10^{-1}
tons/hr	2.5199 x 10^{2}	1.5120 x 10^{4}	9.0718 x 10^{2}	2.1772 x 10^{4}	3.3333 x 10	2.0 x 10^{3}	4.8000 x 10^{4}	1.0	24.0	8.7600 x 10^{3}
tons/day	1.0500 x 10	6.2999 x 10^{2}	3.7799 x 1.0	9.0718 x 10^{2}	1.3889	8.3333 x 10	2.0 x 10^{3}	4.1667 x 10^{-2}	1.0	365.0
tons/yr	2.7756 x 10^{-3}	1.7260	1.0256 x 10^{-1}	2.4658	3.8052 x 10^{-3}	2.2831 x 10^{-1}	5.4795	1.1416 x 10^{-4}	2.7397 x 10^{-3}	1.0

To convert a value from a given unit to a desired unit, multiply the given value by the factor opposite the given units and beneath the desired units.

Appendix D

TOXICITY OF CHEMICAL COMPOUNDS USED IN SOLAR CELL PRODUCTION

This appendix summarizes the toxic hazard ratings, toxic dose and toxic effects for chemical compounds involved in a solar cell manufacturing facility (Refs. 101, 102). The toxic hazard rate code and acronyms are defined, followed by the toxicity for each of the solar cell materials. Several materials are suspected carcinogens (Ref. 103).

For spill hazards and emergency responses, transportation information and production sites, etc., consult the Coast Guard "CHRIS" manuals and the USEPA "CHMTADS" data system (Refs. 104 and 105).

Toxic Hazard Rating Code

0 NONE: (a) No harm under any conditions;
(b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes; not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short exposure to small quantities.

U UNKNOWN: No information on humans considered valid by authors.

Definitions

TXDS: Qualifying toxic dose
TFX: Toxic effects
TWA: Time weighted average
TCLo: Toxic concentration low
TDLo: Toxic dose low
LDLo: Lethal dose low
LD50: Lethal dose fifty.

ALUMINUM COMPOUNDS

Toxic Hazard Rating:

Acute local: 0
Acute systemic: 0
Chronic local: Inhalation 2
Chronic systemic: 0

Aluminum Oxide

Synonym: Alumina
Description: White Powder
Formula: Al_2O_3

TXDS:

Inhalation - mouse TCLo: 157 mg/m^3/60DY

Aluminum Chloride

Description: White granular crystals
Formula: $AlCl_3$

TXDS:

Oral - rat LD50: 3700 mg/kg
Oral - mouse LD50: 3600 µg/kg

ARSENIC COMPOUNDS

Toxic Hazard Rating:

Acute local: Irritant 2; Allergen 2; Ingestion 3
Acute systemic: Ingestion 3; Inhalation 3
Chronic local: Irritant 2; Allergen 2
Chronic systemic: Ingestion 3; Inhalation 3.

Arsenic Acid

Synonyms: True arsenic acid
Description: White, translucent crystals
Formula: $H_3AsO_4 - 1/2\ H_2O$.

Arsenic Trioxide

Synonyms: White arsenic; Arsenic (III) oxide; arsenic sequioxide; arsenous oxide; arsenous oxide anhydride.
Description: White, odorless, tasteless amorphous powder
Formula: As_2O_3.

TXDS:

Oral - human;	LDLo: 1 mg/kg
Inhalation - human;	TCLo: 110 µg (As)/m^3
TFX: skin	
Inhalation - human;	TCLo: 200 µg (As)/m^3
TFX: carcinogen	
Oral - rat	LD50: 45 mg/kg
Oral -	LD50: 43 mg (As)/kg
Oral - rabbit	LD50: 4 mg/kg
U.S. Occupational Standard USOS - air;	TWA: 0.5 mg (As)/m^3
NIOSH Received Standard - air;	TWA: 50 µg (As)/m^3

Arsenic Pentoxide

Synonyms: Arsenic oxide, arsenic acid anhydride
Description: White, amorphous solid
Formula: As_2O_5

TXDB:

Oral - rat	LD50: 8 mg/kg
Intravenous - rabbit	LDLo: 6 mg/kg

Sodium Arsenate

Synonyms: Sodium metaarsenate, sodium ortho-arsenate
Description: Clear, colorless crystals; mild alkaline taste
Formula: $NaAsO_3$

TXDB:

Inhalation - human	TDLo: 4 mg/m^3
TFX - carcinogen	
Intraperitoneal - mouse	LD50: 9 mg/kg
Intraperitoneal - mouse	LDLo: 45 mg/kg

BORON COMPOUNDS

Toxic Hazard Rating:

Acute local: Ingestion 2; Inhalation 4
Acute systemic: 0
Chronic local: 0
Chronic systemic: Ingestion 2; Inhalation 2; Skin Absorption 4

TXDB:

Oral - mouse	LD50: 2000 mg/kg

CADMIUM COMPOUNDS (See also Appendix E)

Toxic Hazard Rating:

Acute local: Irritant 3; Ingestion 3; Inhalation 3
Acute systemic: Ingestion 3; Inhalation 3
Chronic local: Variable
Chronic systemic: Ingestion 3; Inhalation 3

Cadmium

Description: Hexagonal crystals; silver-white malleable metal

TXDB:

Intramuscular - rat	LDLo: 15 mg/kg
Intramuscular - rat	TDLo: 70 mg/kg
Intramuscular - human	LDLo: 25 mg/kg

U. S. Occupational Standard USOS - Air: TWA 200 µg/m^3

Cadmium Oxide

Description: Amorphous, brown crystals; cubic, brown crystals
Formula: CdO

TXDS:

Inhalation - man	TCLo: 9 mg/m^3/5H
Oral - rat	LD50: 72 mg/kg
Inhalation - rat	LC50: 500 mg/m^3
Subcutaneous - rat	TDLo: 90 mg/kg
Inhalation - mouse	LC50: 700 mg/m^3/10M
Inhalation - dog	LD50: 4000 mg/m^3/10M
Inhalation - rabbit	LC50: 4500 mg/m^3/10M
Inhalation - guinea pig	LC50: 3500 mg/m^3/10M

U.S. Occupational Standard USOS - Air: TWA 100 µg/m^3

Cadmium Chloride

Description: Hexagonal, colorless crystals
Formula: $CdCl_2$

TXDS:

Oral - rat	LD50: 88 mg/kg
Intraperitoneal - rat	TDLo: 3 mg/kg/(9D preg)
Subcutaneous - rat	TDLo: 4 mg/kg/(14-17D preg)
Subcutaneous - rat	TDLo: 2.2 mg/kg
Intramuscular - rat	TDLo: 4 mg/kg
Parenteral - rat	TDLo: 2 mg/kg
Inhalation - dog	LCLo: 320 mg/m^3
Subcutaneous - mouse	TDLo: 16 mg/kg (14-17D preg)
Subcutaneous - mouse	TDLo: 6 mg/kg
Inhalation - dog	LC90: 8 mg/m^3/30MC
Subcutaneous - rabbit	TDLo: 9 mg/kg

Cadmium Sulfide

Synonym: Greenockite
Description: Yellow-orange crystals
Formula: CdS

TXDS:

Intramuscular - rat	TDLo: 150 mg/kg
Subcutaneous - rat	TDLo: 90 mg/kg
Intramuscular - rat	TDLo: 250 mg/kg

CHROMIUM COMPOUNDS

Toxic Hazard Rating:

Acute local: Irritant 3; Ingestion 3, Inhalation 3
Acute systemic: Unknown

Chronic local: Irritant 3; Ingestion 3; Inhalation 3
Chronic systemic: Ingestion 3, Inhalation 3.

Chromium Trioxide

Synonyms: Chromium (6O) oxide, chromic acid, chromic anhydride
Description: Dark, purple-red crystals
Formula: CrO_3.

TXDS:

Subcutaneous - dog:	LDLo: 330 mg/kg
Implant - rat:	TDLo: 125 mg/kg
TFX - carcinogen:	

U.S. Occupational Standard USDA - air: TWA: 100 $\mu g/m^3$ ($AsCrO_3$)

Sodium Chromate

Description: Yellow crystals
Formula: Na_2CrO_4.

TXDS:

Subcutaneous - rabbit:	LDLo: 243 mg/kg

Sodium Dichromate

Synonyms: Sodium acid chromate, sodium bichromate
Description: Red crystals
Formula: $Na_2Cr_2O_7 \cdot 2H_2O$

TXDS:

Intermuscular - rat:	TDLo: 140 mg/kg

U.S. Occupational Standards USOS - air: TWA: 100 $\mu g/m^3$ ($AsCrO_3$)

Potassium Chromate

Synonyms: Neutral potassium chromate tarapacaite
Description: Yellow crystals
Formula: K_2CrO_4

TXDS:

Oral - human:	LDLo: 430 mg/kg

Potassium Dichromate

Synonyms: Potassium dichromate, red potassium chromate
Description: Bright, yellowish-red, transparent crystals, bitter metallic taste
Formula: K_2CrO_7
Toxicity: See Chromium Compounds.

Chromic Acid

Synonyms: Chromic anhydride, chromic trioxide
Description: Dark, purple-red crystals
Formula: CrO_3

TXDS:

Inhalation - human TCLo: 110 µg/M

U.S. Occupational Standard USOS - air: CL: 100 µg/m^3 (as CrO_3)

Chromic Acid, Lead Salt

TXDS

Subcutaneous - rat TDLo: 1200 mg/kg
Intraperitoneal - guinea pig LDLo: 400 mg/kg

U.S. Occupational Standard USOS - air: CL: 100 µg/m^3 (as CrO_3)

Chromic Acid, Calcium Salt

TXDS:

Subcutaneous - rat TDLo: 76 mg/kg/30W
Intramuscular - rat TDLo: 95 mg/kg/30W I
Implant - rat TDLo: 63 mg/kg
Subcutaneous - mouse TDLo: 50 mg/kg
Implant - mouse TDLo: 50 mg/kg

U.S. Occupational Standard USOS - air: CL: 100 µg/m^3 (as CrO_3)

COPPER COMPOUNDS

Toxic Hazard Rating:

Acute local: Irritant 1; Allergen 1; Ingestion 1; Inhalation 1
Acute systemic: Ingestion 2; Inhalation 2
Chronic local: Allergen 1
Chronic systemic: Ingestion 1; Inhalation 1

Cupric Oxide

Synonyms: Tenorite
Description: Fine, black powder
Formula: CuO

TXDS:

None available.

Copper Sulfate

Synonyms: Blue vitriol; blue stone; roman vitriol, cupric sulfate
Description: Blue crystals or blue crystalline granules of powder
Formula: $CuSO_4 \cdot 5H_2O$

TXDS:

Oral - rat	LD50: 300 mg/kg
Intraperitoneal - mouse	LD50: 7 mg/kg

U.S. Occupational Standard: USOS - air: TWA 1 mg/m^3 (as Cu)

Copper Carbonate

Synonyms: Copper bicarbonate, cupric carbonate
Description: Green powder
Formula: $CuCo_3$ $Cu(OH)_2$

TXDS:

Oral - rat	LD50: 159 mg/kg

U.S. Occupational Standard: USOS - air: TWA: 1 mg/m^3 (as Cu)

Copper Acetate

Synonyms: Cupric acetate; neutral verdigris
Description: Greenish-blue, fine powder or small crystals
Formula: $Cu(C_2H_3O_2)_2 \cdot H_2O$

TXDS:

Oral - rat	LD50: 710 mg/kg

GALLIUM COMPOUNDS

Toxic Hazard Rating:

Acute local: U
Acute systemic: Ingestion 1
Chronic local: U
Chronic Systemic: Ingestion 1

TXDS:

Subcutaneous - rat	LDLo: 200 mg/kg

Gallium Arsenide

Description: Cubic crystals with dark gray metallic sheen
Formula: GaAs

TXDS:

Oral - rat	LD50: 4700 mg/kg

A recognized carcinogen

Gallium Chloride

TXDS:

Inhalation - rat	LCLo: 191 mg/m^3/3H
Intraperitoneal - mouse	LD50: 57 mg/kg

HYDROCHLORIC ACID

Toxic Hazard Rating:

Acute local: Irritant 3
Acute systemic: Ingestion 3; Inhalation 3
Chronic local: Irritant 3
Chronic systemic: U

TXDS:

Inhalation - rat	LC50: 4701 ppm/30M
Inhalation - mouse	LC50: 2142 ppm/30M
Intraperitoneal - mouse	40 mg/kg
Inhalation - rabbit	LCLo: 4416 ppm/30M
Inhalation - mammal	LCLo: 1000 mg/m^3/2H

U.S. Occupational Standard: USOS - air: CL 5 ppm

LEAD COMPOUNDS

Toxic Hazard Rating:

Acute local: 0
Acute systemic: Ingestion 3; Inhalation 3
Chronic local: 0
Chronic systemic: Ingestion 3; Inhalation 3; Skin Absorption 3
U.S. Occupational Standard: USOS - Air: TWA 200 µg/m^3

Lead Arsenate

Synonyms: Lead o-arsenate; lead di-o-arsenate; lead mono-o-arsenate
Description: White crystals

TXDS:

Oral - rat	LD50: 100 mg/kg
Oral - rabbit	LD50: 121 mg/kg

U.S. Occupational Standard: USOS - air: TWA 150 µg/m^3

Lead Chloride

Synonym: Cotunnite
Description: White crystals

TXDS:

Oral - guinea pig LDLo: 500 mg/kg

U.S. Occupational Standard: USOS - air: TWA 269 $\mu g/m^3$

NITRIC ACID

Toxic Hazard Rating:

Acute local: Irritant 3; Ingestion 3; Inhalation 3
Acute systemic: Inhalation 3
Chronic local: Irritant 4
Chronic systemic: Inhalation 3

TXDS:

Inhalation - rat LC50: 49 ppm/4H

U.S. Occupational Standard: USOS - air: TWA 5 ppm

Nitric Acid, Cadmium Salt

TXDS:

Oral - rat LD50: 300 mg/kg

Nitric Acid, Copper Salt

TXDS:

Oral - rat LD50: 940 mg/kg

U.S. Occupational Standard: USOS - air: TWA 1 mg/m^3 (as Cu)

Nitric Acid, Zinc Salt

TXDS:

Oral - rat LD50: 1190 mg/kg

PHOSPHORUS COMPOUNDS, INORGANIC

Phosphorus

TXDS:

Oral - human	LDLo: 1.4 mg/kg
Subcutaneous - dog	LDLo: 4 mg/kg
Oral - rabbit	LDLo: 10 mg/kg
Subcutaneous - rabbit	LDLo: 15 mg/kg

Phosphoric Acid

Description: Colorless liquid or rhombic crystals

Toxic Hazard Rating:

Acute local: Irritant 2
Acute systemic: Ingestion 2; Inhalation 4
Chronic local: Irritant 2; Inhalation 2
Chronic systemic: U

Phosphine (PH_3)

Synonyms: Hydrogen phosphide; phosphoretted hydrogen
Description: Colorless gas

Toxic Hazard Rating:

Acute local: Irritant 2; Inhalation 4
Acute systemic: Inhalation 3
Chronic local: U
Chronic systemic: Inhalation 3

TXDS:

Inhalation - human	LCLo: 8 ppm
Inhalation - rat	LC50: 11 ppm/4H

U.S. Occupational Standard: USOS - air: TWA 400 $\mu g/m^3$

SELENIUM COMPOUNDS

Toxic Hazard Rating:

Acute local: Irritant 2
Acute systemic: Ingestion 2; Inhalation 2-3

TXDS:

Inhalation - rat	LCLo: 33 mg/kg/8H
Intravenous - rat	LD50: 6 mg/kg

U.S. Occupational Standard: USOS - air: TWA 0.2 mg/m^3

Selenium Dioxide

Description: White to slightly reddish, lustrous, crystalline powder or needles
Formula: SeO_2

TXDS:

Subcutaneous - rat	LD50: 4 mg/kg

U.S. Occupational Standard: USOS - air: TWA 0.2 mg/m^3

SILICON COMPOUNDS

Silicon

TXDB:

Oral - rat	LD50: 2830 mg/kg

Silicon Chloride ($SiCl_4$)

Description: Colorless, fuming liquid, suffocating odor

TXDB:

Inhalation - rat	LC50: 8000 ppm/4H

Silica (Silicon Dioxide)

Synonyms: Silicic anhydride; crystaballite
Description: Colorless crystals

TXDB:

Oral - rat	LD50: 3160 mg/kg
Intravenous - rat	LD50: 15 mg/kg
Intrapleural - rat	TDLo: 200 mg/kg

Silane (SiH_4)

Synonyms: Silicomhydride, disilane
Description: Gas or liquid

TXDB:

Inhalation - rat	LCLo: 9600 ppm/4H

Trichloro Silane ($SiHCl_3$)

TXDB:

Oral - rat	LD50: 1030 mg/kg
Inhalation - rat	LCLo: 1000 ppm/4H

SULFURIC ACID

Toxic Hazard Rating:

Acute local: Irritant 3; Ingestion 3; Inhalation 3
Acute systemic: U
Chronic local: Irritant 3; Inhalation 3
Chronic systemic: U

TXDB:

Inhalation - human	TCLo: 800 $\mu g/m^3$
Inhalation - human	TCLo: 5 mg/m^3/15M
Oral - rat	LD50: 2140 mg/kg

Inhalation - rat	LCLo: 170 ppm/7H
Inhalation - mouse	LCLo: 140 ppm/210M
Inhalation - guinea pig	LCLo: 48 ppm/H

U.S. Occupational Standard: USOS - air: TWA 1 mg/m^3

TIN COMPOUNDS

Elemental tin is not generally considered toxic. Some inorganic salts are irritants or can liberate toxic fumes on decomposition. Organo tin compounds are used as pesticides.

TITANIUM COMPOUNDS

Toxic Hazard Rating:

Acute local: Ingestion 1; Inhalation 1
Acute systemic: U
Chronic local: U
Chronic systemic: U

Titanium Chloride ($TiCl_4$)

TXDS:

Intramuscular - rat	LDLo: 50 mg/kg
Inhalation - mouse	LCLo: 10 mg/m^3/2H
Intramuscular - human	LDLo: 83 mg/kg

Titanium Oxide

Synonym: Rutile
Description: Blue crystals

U.S. Occupational Standard: USOS - air: TWA 15 mg/m^3

ZINC COMPOUNDS

Toxicity: Variable, generally of low toxicity.

Zinc Chloride

Synonyms: Butter of zinc, zinc dichloride
Description: White deliquescent crystals
Formula: $ZnCl_2$

TXDS:

Inhalation - human	TCLo: 4800 mg/m^3
Intravenous - rat	LDLo: 30 mg/kg

Zinc Oxide

Syncnyms: Zincite, chinese white, zinc white
Description: White or yellowish powder

Formula: ZnO

TXDB:

A disinfectant

Inhalation - rat	LDLo: 400 mg/m^3
Inhalation - guinea pig	LCLo: 8500 mg/m^3

U.S. Occulational Standard: USOS - air: TWA 5 mg m^3

Zinc Sulfate

Synonyms: Zinkosite, white vitriol
Description: Colorless crystals
Formula: $ZnSO_4$

TXDB:

Intraperitoneal - rat	LD50: 40 mg/kg
Intraperitoneal - mouse	LD50: 29 mg/kg
Subcutaneous - rabbit	LDLo: 2.5 mg/kg

Appendix E

CADMIUM: PROPERTIES, OCCURRENCE, AND ECOLOGICAL EFFECTS

Chemical and Physical Properties (Refs. 48, 85)

Cadmium metal is a bluish-white to silver-white metal that melts at 321 C and boils at 765 C. Its vapor pressure is 1.4 torr at 400 C and 16 torr at 500 C. Thus, significant losses by vaporization can be expected during metallurgical processing or during accidents such as fires or explosions. In the vapor phase, it is very reactive, quickly forming finely divided CdO in the air.

Cadmium exhibits only valence +2 in its compounds with a tendency to form covalent bonds, especially with sulfur. Alkyl cadmium compounds are very unstable, rapidly reacting with water or moist air under ambient environmental conditions. In water, CdS and $CdCO_3$ are slightly soluble, but it forms a wide variety of soluble complexes, notably with cyanides and amines.

Occurrence

Major sources of atmospheric emissions of cadmium are the smelting of ores, manufacture of metallic alloys, reprocessing of cadmium-plated materials and cadmium-containing alloys, combustion of coal and oil, the burning of cadmium-weighted plastics and of sewage sludge. Estimated rates of emission to air, water and land are given in Table E-1.

Most fresh waters contain less than 1 $\mu g/l$ (Ref. 85), while a typical atmospheric level is reported as 0.025 $\mu g/m^3$ (Ref. 86). High concentrations of cadmium have been reported in the vicinity of major emission sources (Refs. 85 and 87).

Ecological Effects

Cadmium is toxic to most living organisms, including mammals (Ref. 86).

Damage to plants from excess cadmium has been reported, but the required levels of cadmium were greater than even those in soils of contaminated areas.

No evidence exists that cadmium concentrates in marine food chains, but mollusks and plankton-eating birds possess the highest concentrations recorded. Adverse effects on reproduction of fish have been reported at

TABLE E-1. ESTIMATED RATES OF EMISSION OF CADMIUM DURING PRODUCTION AND DISPOSAL OF CADMIUM PRODUCTS FOR 1968 (REF. 85).

					Losses During Use and Disposal			
	Mining and Ore Concentration, tons/yr	Primary Cadmium Production, tons/yr	Electroplating, Pigments and Plastics tons/yr	Coal and Oil Combustion, tons/yr	Cadmium-Plated Metals, tons/yr	Pigment, Plastics, and Miscellaneous tons/yr	Alloys and Batteries, tons/yr	Total, tons/yr
Air Contamination		930		120	500	90	40	1680
Water Contamination	3000	240	300					3540
Land Disposal (Dumps, Land Fills, Slag Pits, Mine Tailings)	300	310		360	500	490	220	2180

moderate concentrations (Ref. 85). In humans, cadmium is concentrated in the kidneys and liver.

Exposure to fumes or dusts of cadmium metal or cadmium oxide is known to cause acute pulmonary edema. Chronic exposure through the respiratory tract produces chronic emphysema. Repeated suggestions have been stated that build-up of cadmium in the body is related to the occurrence of hypertension in man. Rats and rabbits have developed hypertension after ingestion or injection of cadmium (Refs. 85 and 86). Carcinogenic effects have not yet been recognised in humans.

Large doses of cadmium have resulted in itai-itai ("ouch-ouch") disease in Japan. The disease leads to progressive decalcification of bone, with intense joint pain and increased vulnerability to fractures. About 200 cases have been described, of which 100 died (Ref. 86).

Current Regulations

Effluent guidelines for the zinc and lead smelting and refining industries have been promulgated by the Environmental Protection Agency at levels of 0.0027 kg/MT zinc and 0.0004 kg/MT of lead or 0.5 mg/l of discharge water (Ref. 88).

The only air standards in effect for cadmium are those of the Occupational Safety and Health Administration (OHSA). The current OSHA limit is: for fumes, 100 $\mu g/m^3$ (over 8 hours), with a 300 $\mu g/m^3$ short term ceiling; for dust, 200 and 600 $\mu g/m^3$, respectively. Newly recommended OHSA standards are 40 $\mu g/m^3$ over a 15-minute period.